Synthesis of 2,6-dimethylnaphthalene and analogues over solid catalysts.

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Synthesis of 2,6-dimethylnaphthalene and analogues over solid catalysts

by

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy by the University of Wales Swansea

September 2005

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Acknowledgements

Firstly, I would like to thank my supervisor Professor Keith Smith, for his enthusiasm, encouragement and invaluable advice. Thanks also to Dr. Simon Roberts and all concerned at DPT for their financial assistance, loan of equipment and useful discussions. Thanks to the University of Wales Swansea for the financial assistance during the course of my studies.

Thanks must also go to other members of the chemistry department at Swansea. My work colleagues in G3, particularly Gamal for always knowing the answer and who's love for the subject is an inspiration. Amany, Mark, Mu, Zhiang, and Des. A big thanks to all technical staff including; Ian, Stan, Alf, Jon Tregembo, Jon Lewis, Mike Turner, Myron and Gareth Llewellyn. Not forgetting Margaret and Eilen for all they have done for me.

A big Cheers to tea room buddies old and new Joey, Jon T, Kath, Trystan, Rachel, Handle, Vic, Claire and Swadipa. A big thank you to Peter and Mike for their endless sources of entertainment and making the best cup of cha in Swansea! I will miss you all! Thanks to the almighty Gusto's, Little Jogger and Stevie G and the Palmers, Kay and Craig for always bringing the fun times to Swansea, and helping me go LARGE! no matter what city or country we happen to be in!! Thanks also to my oldest friend Emma, for her constant flow of cards when I needed cheering up and to Carol and Dave the rave for food packages, lifts home and pink presents.

A big thank you to my wonderful family; my brother who will be pleased that I am finally joining the real world and paying my taxes! To Nana Nancy, Bamper Len, Nana Beryl and Bamper Vernon, for their endless support and much needed financial assistance. A special thanks to my wonderful parents, for the special teas extra funds and for always believing in me. Thank you both for getting me through it.

Finally, the biggest thanks of all must go to Big Chris. My very own 6ft 5 pillar of strength. You are a truly remarkable person, and your generosity, patience and kindness never ceases to amaze me. Thank you for making everything more bearable. Chelsea for the treble next year!!

So, I guess that's it! Let the good times roll!

In loving memory of my beautiful mother Julie

I did it Mam!

Summary

Chapter 1

The first part of Chapter 1 highlights the advantages and uses of heterogeneous inorganic solids as catalysts. A brief review of various microporous and mesoporous solids that have been employed as catalysts is given.

The second and third parts of Chapter 1 focus on the importance of 2,6-dialkylnaphthalenes in the commercial synthesis of polyethylenenaphthalate. Past and present methods for producing 2,6-dialkylanaphthalenes is also discussed.

Chapter 2

Chapter 2 describes the attempted three stage synthesis of 2,6-dimethylnaphthalene from *p*-xylene and crotonic acid using zeolite catalysts. It was found that the zeolite catalysts were not sufficiently active to facilitate the reaction.

Chapter 3

Chapter 3 describes the alkoxyalkylation of naphthalene over zeolite catalysts to obtain an intermediate for use in the production of polyethylenenaphthalate. The main body of work focuses on the optimisation of the methoxymethylation of naphthalene. When protonated zeolite mordenite was employed under optimised conditions, a 45 % yield of mono(methoxymethyl)naphthalene with a 2/1 of 3.0 and a 45 % yield of bis(methoxymethyl)naphthalene with a 2,6/2,7-ratio of 17.0 were observed. The major isomer was found to 2,6-bis(methoxymethyl)naphthalene.

Chapter 4

Chapter 4 describes the methoxymethylation of naphthalene over protonated zeolite mordenite. Under optimised conditions, a 57 % yield of bis(methoxymethyl)naphthalene with a 2,6/2,7-ratio of 9.7 were observed. 2,6-bis(methoxymethyl)naphthalene was the major isomer observed.

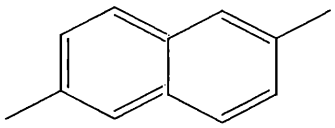
Chapter 5

Part 1 of Chapter 5 focuses on the ethoxymethylation of naphthalene over protonated zeolite mordenite zeolite. Under optimised conditions, (ethoxymethyl)naphthalene was observed in a 19 % yield with a 2/1 ratio of 9.9.

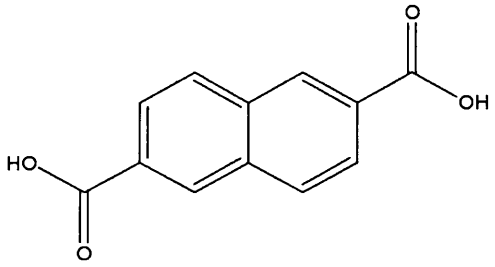
In Part 2, the ethoxymethylation of 2-(ethoxymethyl)naphthalene is discussed. A 26 % yield of bis(ethoxymethyl)naphthalene was observed under optimised conditions. Only one bis(ethoxymethyl)naphthalene isomer, which was thought to be the desired 2,6- isomer, was observed.

Abbreviations

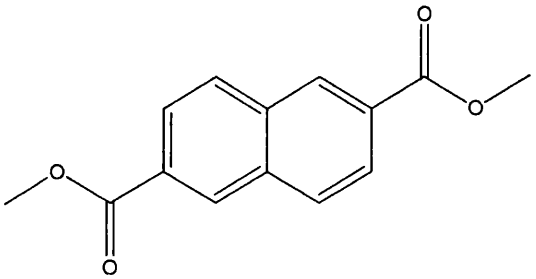
2,6-DMN: 2,6-dimethylnaphthalene



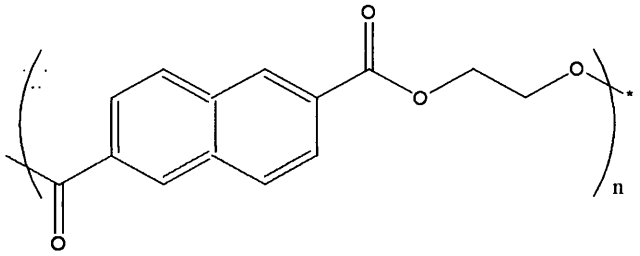
2,6-NDA: 2,6-naphthalenedicarboxylic acid



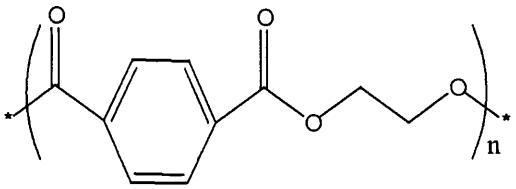
2,6-NDC: 2,6-naphthalenedicarboxylate



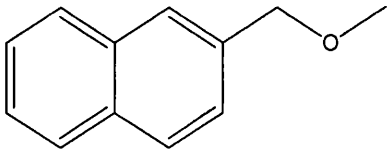
PEN: Polyethylenenaphthalate



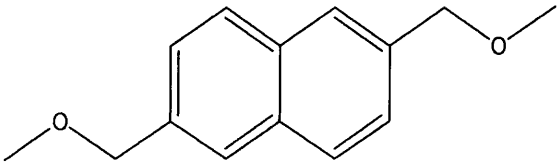
PET: Polyethyleneterephalate



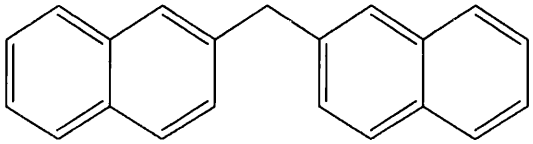
2-MMN: 2-(Methoxymethyl)naphthalene



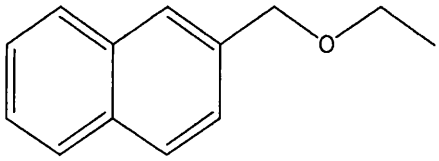
2,6-Bis(MM)N: 2,6-Bis(methoxymethyl)naphthalene



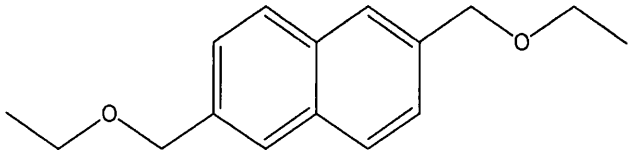
MBN: Methylenebis(naphthalene)



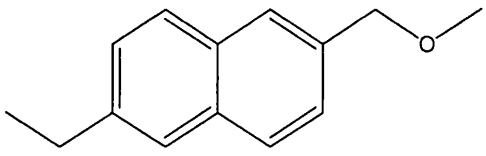
2-EMN: 2-(Ethoxymethyl)naphthalene



2,6-Bis(EM)N: 2,6-Bis(ethoxymethyl)naphthalene



2,6-Et(MM)N: 2,6-Ethyl(methoxymethyl)naphthalene



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Chapter 1, Part 1

Inorganic Solids as Heterogeneous catalysts

1.1.1 Introduction[1-4]

In the last few decades there have been increasingly stringent environmental regulations and an increased pressure on chemical industry to minimise the environmental implications of chemical processes.

Waste minimisation not only benefits the environment but may lower the cost of chemical processes and raise performance. In view of this, the use of heterogeneous catalysts has become very attractive, since they are reusable, easy to separate and generally environmentally benign.

This Section briefly reviews heterogeneous inorganic solid catalysts and the role they play in industry. The different types of inorganic solids used as heterogeneous catalysts and their properties will also be discussed.

1.1.2 Introduction to catalysis[6-13]

A catalyst is described as a substance that is not consumed in a reaction but can increase the rate of reaction. There are two main types of catalysts; a homogenous catalyst (in the same phase as the reactants) and a heterogeneous catalyst (in a different phase to the reactants).

The structure and properties of heterogeneous catalysts offer many advantages over homogenous catalysts. They can be easily separated and are generally insoluble, non-toxic, odourless, non-volatile and can generally be reused.

1.1.3 Types of Inorganic solids[5]

Inorganic solids have found substantial use as heterogeneous catalysts and they are generally split into three types according to their structure.

- The solid is amorphous, with random impervious pore or pitted openings. Silica and alumina are examples of inorganic solids which exhibit this type of structure.

- The solid has a lamellar structure, comprising of impervious sheets or layers, separated by open regions where a reaction is most likely to occur. Clays are examples of inorganic solids which exhibit this type of structure.
- The solid has a repeating 3-dimentional structure comprising a regular array of channels. Reactions can occur within the channels of the solid, but is dependent on the dimensions of the channel and reactant species (shape selectivity). Zeolites are examples of inorganic solids which exhibit this type of structure.

Part 1 of this Chapter briefly reviews the characteristic properties and applications of these solid acid catalysts.

1.1.4 Silica[5,12-15]

Silica or silicon dioxide (SiO_2), exists in various polymorphic forms including hydrated and anhydrous crystalline, microcrystalline and amorphous forms. The structure of silica is made up of Si^{4+} cations tetrahedrally coordinated to O^{2-} anions. Siloxane bridges (Si-O-Si) connect the tetrahedral sub-unit to create chains, rings, sheets (**Figure 1.1.1**) or three-dimensional assemblages (e.g. zeolites). Silinol (Si-OH) groups are formed from unshared tetrahedral apices and are found at an edge or fault as a result of a breakdown of the pattern of crystallinity. These groups are weakly acidic.

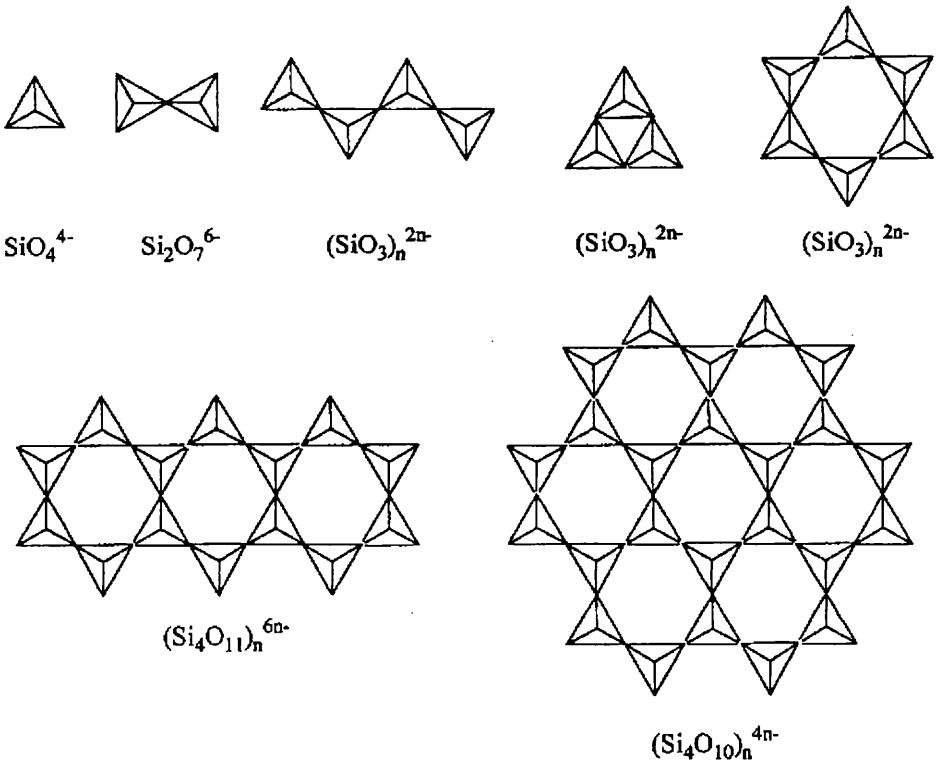

Figure 1.1.1: Examples of tetrahedral silica sub-units creating chains, rings and sheets[5].

Crystalline silicas have a low porosity, therefore they are not used as catalysts. Amorphous silicas can be split into two forms; high-density vitreous silicas (e.g. glass) or low density amorphous silicas (e.g. fumed silica, silica gel, silicic acid).

Low-density amorphous silicas have a high surface area and porosity, and also have a number of faults which make them weakly acidic. Therefore, they are typically employed as sorbents and catalyst supports.

1.1.5 Alumina[5,12-15]

Alumina (Al_2O_3) is synthesised commercially from the mineral Bauxite using the Bayer process. Aluminas are generated in both hydrated and anhydrous polymorphous forms. Examples of hydrated aluminas include aluminium trihydrates ($Al(OH)_3$, equivalent to $Al_2O_3.3H_2O$) and aluminium monohydrate (AlO(OH) equivalent to $Al_2O_3.H_2O$.).

In general, there are two main forms of anhydrous aluminas, α-alumina and γ-alumina. α-Alumina is the only naturally occurring anhydrous alumina (corundum). It has an ordered three-dimensional framework structure, therefore it has high density, mechanical strength, thermal stability, low surface area and low porosity. Essentially, α-alumina is chemically inert and is commonly employed as a low-surface area catalyst support, especially when harsh reaction conditions are required.

γ-Alumina is thermally stable, has a high surface area, large mesopore (20 Å) volume and strong surface acidity. These structural properties make γ-alumina a valuable catalyst in many applications. For example, it is used as a bifunctional support for platinum in platforming (platinum reforming) catalysts.

Activated aluminas can be generated by flash calcination of hydrated aluminas (which results in the explosive release of steam) to give a material which has a high surface area and high porosity. Activated aluminas are amphoteric (containing either acid or basic sites of varying strength) and are typically used as supports.

1.1.6 Synclyst[5,12-16]

Synclysts are amorphous silica-aluminas which exhibit higher acidity than either pure silicas or pure aluminas. They are formed when Si^{4+} in silica is substituted with Al^{3+} in a tetrahedral site, which results in the formation of an acidic hydroxyl group. $[(AlO(OH))_x(SiO_2)_{1-x}]$. The amount of aluminium determines the acidity of Synclysts. These solid acids were used on a large scale as cracking catalysts before the introduction of zeolites. Currently, Synclyst 13 (13 % Al_2O_3: 87 % SiO_2) and Synclyst 25 (25 % Al_2O_3: 75 % SiO_2) are most commonly used.

1.1.7 Clay[5,12-15,17]

Clays are silicates with lamellar (layered) structures which are made up of crystalline sheets derived from tetrahedrally and octahedrally layered systems. They have been employed as solid acids, inert supports and fillers and were one of the earliest catalysts to be employed in cracking

Tetrahedral Layers: Tetrahedron layers are made up of continuous sheets of silica tetrahedral in a hexaganol arrangement. Each tetrahedron is formally centered with a Si^{4+} ion with an O^{2-} ion at each apex, with three oxygens in each tetrahedron being linked to an adjacent tetrahedral.

Octahedral Layers: Octahedral layers are made up of flat layers of edge-sharing octrahedra. Each octrahedra formally contains a cation (typically Al^{3+} or Mg^{2+}) with OH^- or O^{2-} anions at its apices (OH^- apices are not shared whereas the O^{2-} apices are shared with another cation). Octrahedral layers are termed trioctahedral if all the octahedral sites are occupied typically by divalent cations (e.g.Mg^{2+}); whereas in dioctahedral layers two–thirds of the octahedral sites are occupied typically by trivalent cations (e.g.Al^{3+}).

Clays can be categorised into four main types which are defined by the arrangement of the tetrahedrally and octahedrally layered systems (shown in **Figure 1.1.2**).

- **1:1 (or TO) sheets** are composed of one tetrahedral and one octahedral layer
- **2:1 (or TOT) sheets** are composed of two tetrahedral layers and one octahedral layer
- **2:1:1 sheets** are composed of alternanting 2:1 sheets
- **2:1 "inverted ribbon" clays** are essentially 2:1 sheets with inverted tetrahedra cross-linked to octrahedral layers

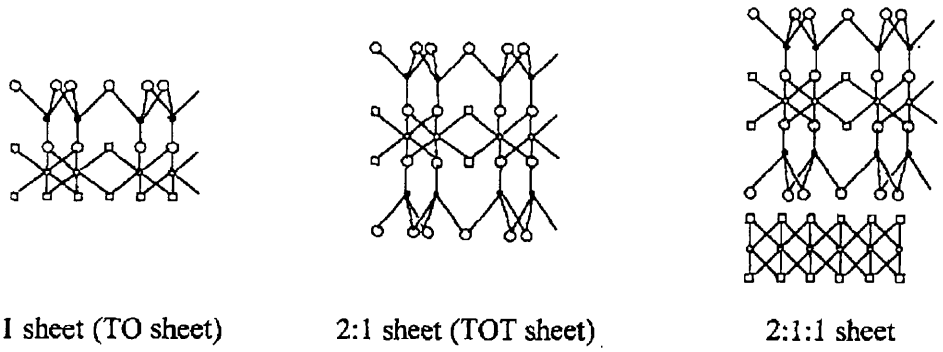

Figure 1.1.2: Examples of layer structures of clay minerals. Si (•), Al ($_o$), O (o), OH (□), H_2O (★)[5].

1.1.7.1 Isomorphous substitution[5]

As illustrated with Synclyst catalysts, clays can undergo isomorphous substitution of Si^{4+} by Al^{3+}. Furthermore, in trioctahedral clays substitution of Mg^{2+} with other divalent and univalent cations can occur and in dioctahedral clays, substitution of Al^{3+} cations with divalent or trivalent cations is observed (common in 2:1 structures).

The isomorphous substitutions gives rise to a net negative charge which can be balanced with interlamellar cations which reside between the negative sheets. These cations can readily undergo exchange to give clays with different properties. Isomorphous substitution only occurs to a small extent in clays with 1:1, 2:1:1 and 2:1 "inverted ribbon" structures, therefore they have low layer charge and low concentrations of interlamellar cations. The isomorphous substitution varies greatly in clays with a 2:1 structure, therefore they can have high layer charges (e.g. micas) and low layer charges (e.g. talc or pyrophyllite). The properties of 2:1 clay minerals is largely dependent on the degree of substitution.

1.1.7.2 Swelling properties of clay[5]

Clay minerals have the ability to absorb water (and other molecular or ionic species) between their layers (intercalcination) which causes the clay to swell as the layers part. This is advantageous if the clay was employed as a catalyst, since the swelling of the clay permits entry to reactants allowing access to active acid sites between the layers. The ability to absorb guest molecules can be dependant on the layer charge and interlamellar cations. Swelling occurs readily in 1:1 clay minerals since water forms strong hydrogen bonds with hydroxyl groups on hydrophilic octahedral layer surfaces. Conversely, in 2:1 clay minerals there are only a small number of surface hydroxyl groups, therefore the ability of interlamellar cations to

become solvated will determine the swelling ability of the clay. Clay minerals with 2:1 structures and low layer charge do not swell readily, and those with 2:1 structures with high layer charges are prevented from swelling because of the presence of strong electrostatic forces which hold the interlayer cations and anionic layers together. Thus, the ability of 2:1 clays to swell is limited to smectites which have an intermediate range of layer charges. Generally, the swelling properties of clay minerals are dependant upon layer charge and the types of interlayer cations present.

1.1.7.3 Acidity and cation exchange [5,14,6]

Interlamellar cations in clay minerals have the ability to exchange with cations from external solutions, with smecites exhibiting the greatest cation exchange capacity (structural defects at layer edges give rise to additional cation exchange capacity). Preparation of acidic, proton exchanged clay minerals can be achieved by exchange NH_4CL to give the ammonium exchanged clay. On calcination NH_3 is lost to give the proton exchanged acidic clay.

The nature and exchange ability of interlamellar cations largely determines the acidity of clay minerals, with clays possessing strong Brønsted acidity if the interlamellar cations are protons or polarising cations (Al^{3+}). In addition, clays have weaker Brønsted and/or Lewis acidity resulting from layer surface and edge defects which can be increased by acid leaching or heat treatment.

1.1.7.4 Pillaring[5,18,20]

The swelling of clays can occur in solvents which can significantly reduce their shape selectivity. In Pillared smectites the layers of the clay are separated and have a more rigid structure with a higher surface area and shape selectivity, they have therefore found more applications in catalysis.

The layers are separated with large cationic species (clusters), by exchange followed by calcinations. The cations act as pillars between the layers to create a uniform 2-dimensional micropore system between layers. Pore sizes of the clay which allow access to guest molecules are determined by the number, height and distance between the pillars.

Aluminium chlorhydrol ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]7^+$) also known as the Keggin cation is commonly used as a pillar it has strong Brønsted acidity (it is acidic in aqueous solution) and a limited ability to swell further.

1.1.8 Zeolites[21-54]

Zeolites are microporous (i.e. pores are less than 20 Å) aluminosilicates, that occur naturally or are made commercially for specific uses. The zeolite structure comprises large voids and channels. Due to the unique porous properties of zeolites, they have extensive and invaluable applications in commercially important process, with a global market of several million tonnes per annum. Zeolites are employed in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents.

Synthetic zeolites were first found to be active and selective catalysts in the isomerisation of hydrocarbons by Rabo *et al.* in 1960[a]. Subsequently, the advantages of using zeolites in other reactions was found. Zeolite catalysis still creates a lot of interest, and are probably the most widely used catalysts in industrial processes. Zeolites form the basis of this review of solid catalysts, and are discussed at length in the subsequent sections.

1.1.8.1 History[21-24]

In 1756, the first zeolite, Stilibite, was discovered by Baron A. F. Cronstedt a Swedish chemist. He found that the mineral lost water rapidly on heating and seemed to boil (the ready loss of water is described as intumescence). The name "zeolite" comes from the Greek words *zeo* (to boil) and *lithos* (stone).

It was discovered by Damour in 1840, that water loss in zeolites was reversible and that zeolites could be rehydrated. In 1925, Weigel and Steinhoff reported on the selective adsorption properties displayed by zeolites. It was found that only certain hydrocarbons could be absorbed by zeolites (larger hydrocarbons were not absorbed). Therefore, zeolites were termed molecular sieves, having the ability to separate molecules according to their size. In the late 1940's, the first study for the use of naturally occurring zeolites was undertaken (in the separation of gases), by the Linde Division of the Union Carbide Corp. They were also the first to prepare synthetic zeolites (e.g. faujasite). Currently, there are over 100 synthetic zeolites with no known counterpart and 39 naturally occurring zeolites. Naturally occurring zeolites can be formed from volcanic debris and are probably the most abundant mineral species on this planet. An example of a natural zeolite is clinoptilolite, and is commonly used as an additive in animal feed. It prolongs the activity of fertilizers by effectively storing ammonium and potassium ions. In industrial processes, the use of synthetic zeolites are favoured over natural zeolites. This stems from the fact that naturally occurring zeolites can contain impurities and can have an irregular framework.

1.1.8.2 Zeolite structure[5,19,16-17,19]

In general, the framework structure of a zeolite is made up of 3-D arrangements of $[SiO_2]$ and $[AlO_2]^-$ tetrahedra (i.e. formally Si^{4+} or Al^{3+} at the centre of

a tetrahedron with O^{2-} at each apex) These are known as primary building units (PBUs) and Si^{4+} and Al^{3+} are referred to as T-atoms. The PBUs are assembled together so that the oxygen at each tetrahedral corner is shared with another tetradron. **Figure 1.1.3** illustrates how secondary building units (SBUs) are formed from a collection of PBUs through corner sharing. A central tetrahedral atom (Si^{4+} or Al^{3+}) is found at each corner.

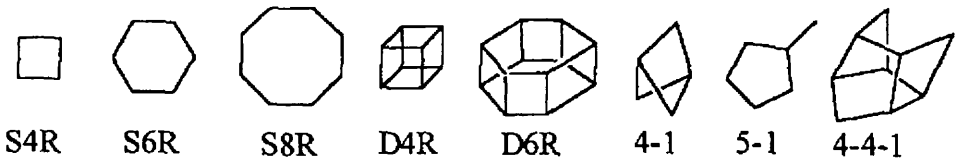

Figure 1.1.3: Zeolite secondary building units (SBUs)[5]

SBUs can then be arranged in different ways to construct polyhedral cages and channels, as illustrated in **Figure 1.1.4**

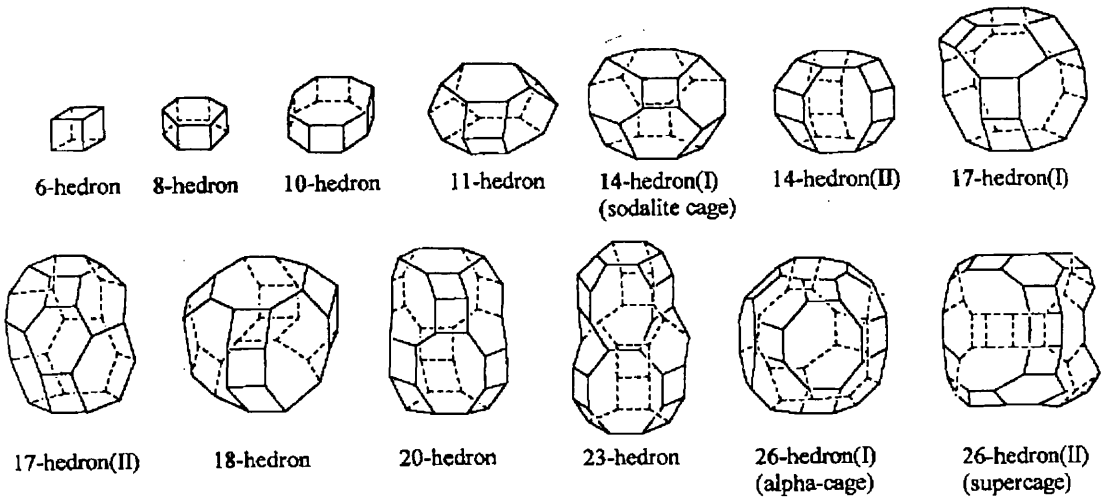

Figure 1.1.4: Zeolite polyhedral cage structures[5]

Polyhedral cages are connected to each other by their faces or interconnecting channels, to create uniform intracrystalline 3-D porous networks. Cavities from spaces or voids can be generated between polyhedra. For example in zeolite HY the intracrystalline voidage can be as high as 50 %. As a result, zeolites have a low bulk density.

Guest molecules can accommodate the voids within the zeolite framework. The size of the pore apertures of a particular zeolite determines the size of the guest molecules that can be adsorbed by the zeolite. If the guest molecule is of similar molecular dimensions to the apertures of the zeolite, then diffusion will be slow. This is not a problem for large pore zeolites such as faujasites, where the 3-dimensional pore structure allows easy diffusion of the guest molecules. The counter-transport of molecules exiting the pores also effects the sorption of a guest molecule into the zeolite framework. In addition, there are strong interactions between guest molecules and cations which can effect the transport of molecules within the zeolite framework[26]. The exact process is not fully understood, but can be rationalised in terms of the principles given below.

Molecular diffusion: This term applies to large pores, where molecules are smaller than the pores and interactions between molecules predominate.

Configurational diffusion: This term applies to pores having molecular dimensions, where molecules are tight within the pores and apeture size is the dominant factor.

Knudsen diffusion: This term applies to small pores, where movement of the molecules is restricted and the interaction with the pore walls predominate.

1.1.8.3 Confinement effects

The reactivity of adsorbed molecules is influenced by the framework structure of the zeolite. The confinement effects within a zeolite was introduced by Derouane[27] in the 1980's. This concept stems from van der Waals interactions. Constraints resulting from the interaction of adsorbed molecules with the channels/cages within the zeolite framework are short range repulsions. These interactions give rise to molecular shape selectivity. Whereas, confinement effects result from longer range forces of attraction (i.e. van der Waals interactions).

Adsorption is favoured for certain molecules, where the selectivity of the zeolite is largely governed by attractive interactions as apposed to the restrictions (shape and size of pores etc) of the zeolite framework. Thus, zeolites act as solid solvents, with sorbed species solvated by the zeolite framework (analogous to normal solute-solvent interactions).

Ultimately, the possibility of a reaction occurring is improved, both because there is a higher concentration of the reactant within the pore, and the transition state of the sorbed reactant is stabilised by the zeolite framework.

1.1.8.4 Classification of zeolites[5]

The classification of zeolites is dependant on the number of T-atoms that the pore apertures are created from. zeolites with apertures containing a maximum of 8 T-atoms are classed as small pore zeolites. zeolites with apertures containing a maximum of 10 T-atoms are classed as medium pore zeolites, and zeolites with apertures containing a maximum of 12 T-atoms are classed as large pore zeolites. In addition, zeolites can have different size pores. For example, Mordenite has both 8 and 12 T-atom apertures. The next section introduces examples of commonly used synthetic zeolites and their applications in industrial processes.

1.1.8.5 Preparation of synthetic zeolites

Zeolites are typically prepared by the hydrothermal treatment of aluminosilicate gels in the presence of an organic template. The zeolite is created around the template, which acts a s a "void filler". For example, zeolite β is synthesised using templates such as the 1,1-dibenzyl-1,1-dimethylammonium ion and the tetraethylammonium ion. The characterisation of zeolites is generally carried out by X-ray diffraction (XRD).

1.1.8.6 Small pore zeolites (maximum 8-T atom apertures)

Zeolite A[5,15,23,28-32]

The first zeolite to be synthesised and fully characterised was zeolite A. It has no natural counterpart and a general empirical formula $Na_{12}Al_{12}Si_{12}O_{48}.27H_2O$). The 6-hedron (D4R SBU) and 14-hedron(I) (sodalite cage) polyhedral cage structures are linked together through bridging oxygens for form a 3-D unit cell structure, as illustrated in **Figure 1.1.5**. The central cavity of the unit cell is an alpha-cage which is 3-dimensionally accessible (26-hedron(I)).

There are six apertures arranged in a cube, which compose of 8-T atoms with pore diameters of 4.3 Å. The sodium ions are either situated at the 6 T-atom rings of the sodalite cage or at the centre of the 8 T-atom apertures of the alpha cage. As a result, the pore volume and width are reduced.

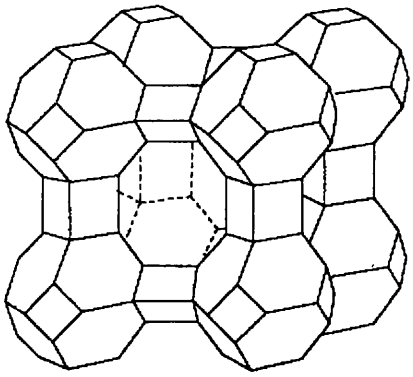

Figure 1.1.5: Structure of zeolite A (eight 14-hedron(I) cages and twelve 6-hedron cages)[5]

The pore width is dependent on the type of cation present. For example, in sodium zeolite A, all access to the cages is blocked. This is because Na^+ cations occupy all eight 6-T rings, three 8-T rings and one offset 4-T ring. Type A zeolites consist of 3A (K^+ cations), 4A (Na^+ cations) and 5A (Ca^{2+}) which are available commercially.

The 8-T ring apertures allow the diffusion of molecules with small kinetic diameters to enter the alpha cages (inscribed diameter 1.14 nm). For example, linear hydrocarbons can enter the porous network, whereas branched hydrocarbons and aromatic compounds are restricted. In view of this, the main industrial application of zeolite A is in purification and separation processes.

1.1.8.7 Medium pore zeolites (maximum 10-T atom apertures)

ZSM-5[5,15,23,28-33]

ZSM-5 is a medium pore synthetic zeolite (10 T-atom apertures with pore diameters of 6.3 Å) with the general empirical formula $Na_3Al_3Si_{93}O_{192}.16H_2O$.

The structure of ZSM-5 is composed of rings made up of five silicon atoms and is therefore referred to as a pentasil zeolite (illustrated in **Figure 1.1.6**). Cross-linked chains of the pentasil subunits make up the framework structure of ZSM-5. Void space outside the pentasil framework creates a 3-D interconnecting system of 10-T ring channels.

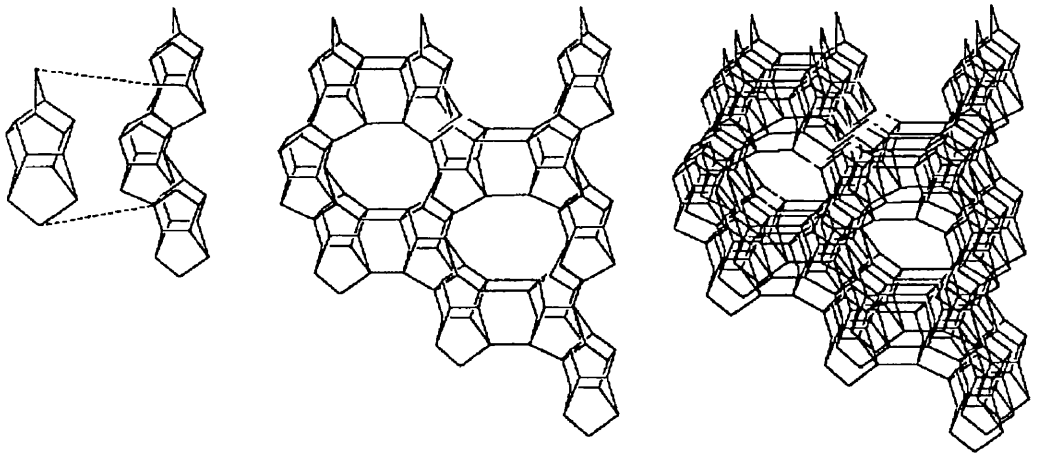

Figure 1.1.6: **1.** Defining the pentasil sub-unit in the ZSM-5 repeating unit. **2.** Arrangement of sub-units to form the apertures. **3.** Stacking to generate the pore system[5]

Two types of interconnecting channels are generated each with oval cross-section (shown in **Figure 1.1.7**). Straight, near circular channels (dimensions of 5.4 x 5.6 Å) run in parallel, and are vertically intersected by a set of sinusoidal (zigzag) channels (dimensions 5.1 x 5.6 Å). The diameter of the channels of ZSM-5 allows it to act as a molecular sieve. For example, ZSM-5 is used in the commercial separation of important organic molecules such as xylenes and branched alkanes.

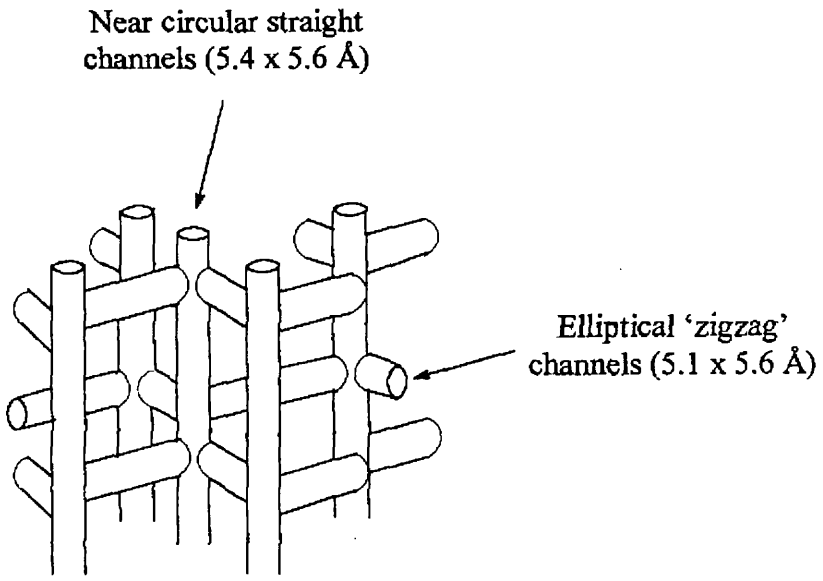

Figure 1.1.7: Pore network of ZSM-5[5]

1.1.8.8 Large pore zeolites (maximum 12-T atom apertures)

Zeolite X and Y (faujasite) [5,15,23,34-35]

Zeolite X and Y (synthetic form of the rare mineral faujasite) are large pore zeoltes with 12-T ring apertures (pore size of 8.0 Å).

Both zeolite X and Y have the same crystalline structure, but with different Si/Al ratios. Zeolite X has a Si/Al ratio of 1.0-1.5 and zeolite Y has a Si/Al ratio greater than 1.5. Zeolite X has a typical empirical formula $Na_{86}Al_{86}Si_{106}O_{384}.264H_2O$, and zeolite Y has a typical empirical formula $Na_{56}Al_{56}Si_{136}O_{384}.250H_2O$.

As shown in **Figure 1.1.8,** the structure of the 3-dimensional framework unit cell is made up of 14-hedron(I) (sodalite cage) cages interlinked with 8-hedron cages (D6R SBUs). This arrangement creates supercages with 12-T atom apertures (7.4 Å diameter). The unit cell structures can face link to create a 3-dimensional pore structure with 12 T-atom entry.

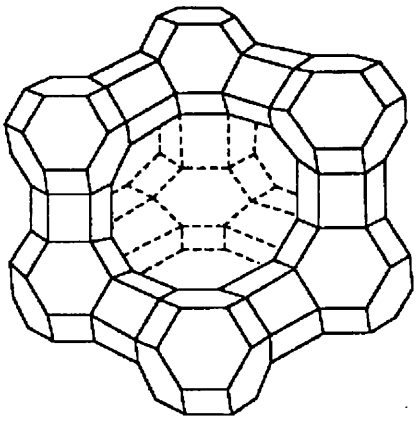

Figure 1.1.8: Structure of faujasites X and Y[5]

Zeolite Y is considered to be one of the most important zeolites manufactured. It is used largely as an additive in powdered detergents where it acts as a builder. Zeolite Y is also a very valuable catalyst and is widely used in catalytic cracking.

Zeolite X is widely used in purification processes (i.e. carbon dioxide removal from gas streams).

1.1.8.9 Mordenite (large pore zeolite)[5,9,17,30-32]

Mordenite also contains 12-T rings and has a typical empirical formula $Na_4Ca_2Al_8Si_{40}O_{96}.n.H_2O$ (high silica content). It is a naturally occurring zeolite and can also be synthetically prepared. It is a large pore zeolite but it differs from zeolites X and Y as it has a 2-dimensional channel system. The structure is created from linking 5-1 SBUs to form channels with both 8-T rings (diameter of 2.6 x 5.7 Å) and 12 T-rings (diameter of 6.5 x 7.0 Å). Although, smaller diameters are generally found in naturally occurring mordenite due to stacking faults. Mordenite has found applications in the petrochemical industry, such as the isomerisation of xylene.

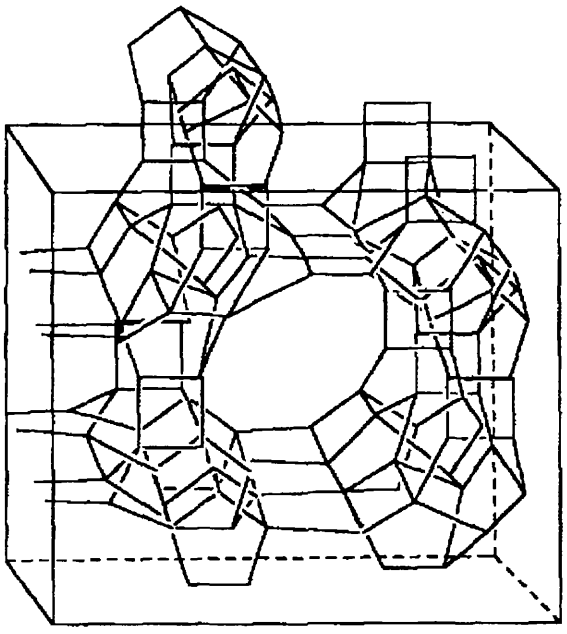

Figure 1.1.9: Structure of mordenite [5a]

1.1.8.10Zeolite β (large pore zeolite)[5,15,23,39-44]

Zeolite β was first synthesised by Wadlinger et al. in 1967. It is a large pore zeolite with a complex structure. A 3-dimensional porous network made up of linked 5-1 SBUs to forms 12-T channels (**Figure 1.1.10**). The channels have two pore diameters (7.0 x 6.4 Å and 5.5 x 5.5 Å) and run in two directions (*a* and *b directions*). The third 12 T-atom channel system is more twisted and runs in the third direction (*c direction*). In an addition, zeolite β is polymorphic, with three different polymorphic structures, A (which has a chiral channel system, B and C. Polymorphs A and B contain similar layers from the same tertiary building unit but are stacked in different ways (A and B are in roughly equal proportions in the structure) . Polymorph C is less stable and is based on a different stacking sequence.

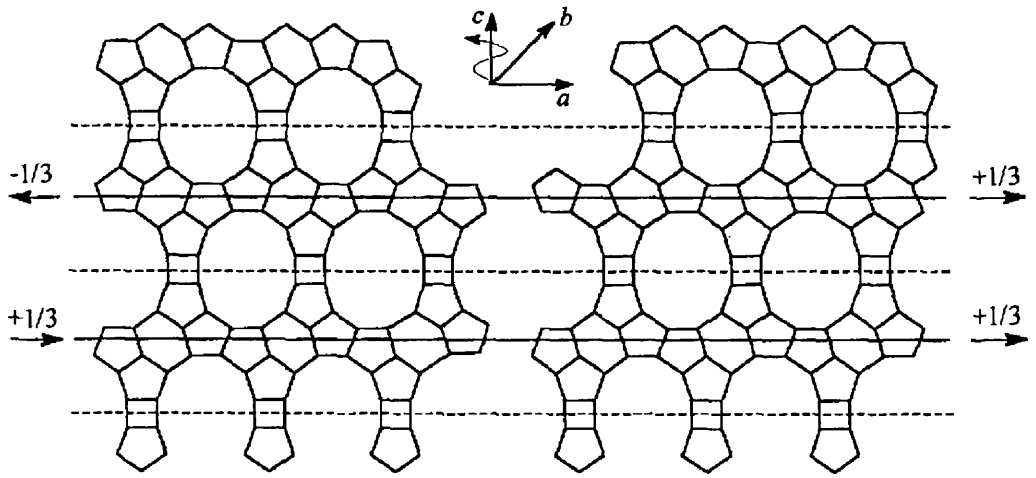

Figure 1.1.10: Polymorphs A and B in zeolite β[5]

There is an equal probability of polymorphs A and B interconnecting with each other when forming layers. Consequently, stacking faults are common in zeolite

β. This does not block or change the topology of the straight channels, but affects the twisting of the channels in the *c* direction. The stacking faults do not effect the catalytic performance of zeolite β, and it is employed in a variety of oil refining processes.

1.1.8.11 UTD-1[15,23,45-48]

UTD-1 (University of Texas at Dallas number 1) is a high-silica, large pore zeolite with 14-T rings and a one-dimensional channel system. It is the first known zeolite to have a pore structure greater than 12-T rings, with pore dimensions of 10 x 7.5 Å (**Figure 1.1.11**). In addition to the large pore dimensions, UTD-1 has comparable strength Brønsted acid sites to other aluminium containing high-silica zeolites and thermal stability up to 1000 °C. Therefore, it has potential as a catalyst in the petroleum industry.

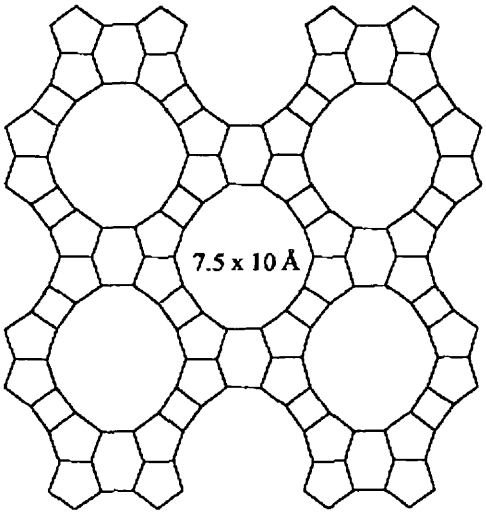

Figure 1.1.11: Framework structure of UTD-1[5]

1.1.8.12 M41S molecular sieves (extra-large pore zeolites)[49-51]

M41S mesoporous molecular sieves were discovered by *Beck et al.* in 1992, at the Mobil Corporation. They have an ordered arrangement of uniform pore openings with pore diameters in the range of 15-100 Å. The pores can be ordered in a hexaganol (MCM-41), cubic (MCM-48) or lamellar arrangement, however the preparation and thermal instability of the cubic and lamellar materials is difficult MCM-41 (**Figure 1.1.12**) is the most commonly studied mesoporous zeolite and has been employed as a catalyst in the cracking of olefins[50].

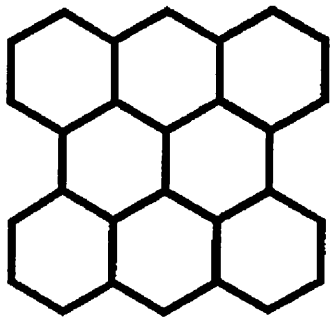

Figure 1.1.12: Structural model of MCM-41[5]

1.1.8.13 Framework composition of zeolites[5]

The framework composition of zeolites is largely dictated by the isomorphous substitution, intercalation, impregnation and cation-exchange. Isomorphous substitution occurs between silicon and aluminium and the extent of the substitution is expressed by the Si/Al ratio in aluminosilicate zeolites. The lowest Si/Al ratio that can be achieved is 1. This is governed by Lowensteins's rule, which disallows Al-O-Al-tetrahedron linkages within the zeolitic structure[26,53]. Furthermore, Dempsey's rule

states that there should be a minimum number of Al/Al pairs in the second nearest neighbour (i.e. Al-O-Si-O-Al)[54-55].

1.1.8.14 Lewis and Brønsted acidity of zeolites[5,20,30]

Zeolites are used extensively as solid acid catalysts in numerous reactions. The acidity of zeolites is typically introduced by cation-exchange with framework cations (e.g. ammonium cations), as illustrated in **Figure 1.1.13**.

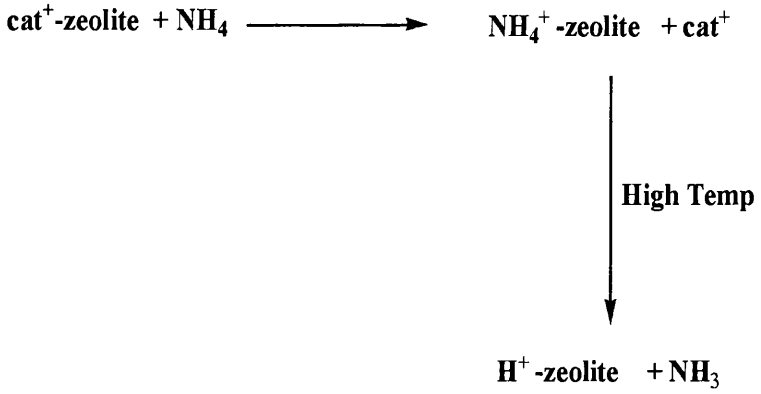

Figure 1.1.13: Generation of protonated zeolites by ammonium cation exchange and calcinations, where cat^+ is a non-framework cation[5].

The removal of ammonia by calcination (heating at a high temperature) produces the proton exchanged zeolite. The protons are present within the zeolite structure as non-framework cations (Brønsted acid sites). This is shown in **Figure 1.1.14.**

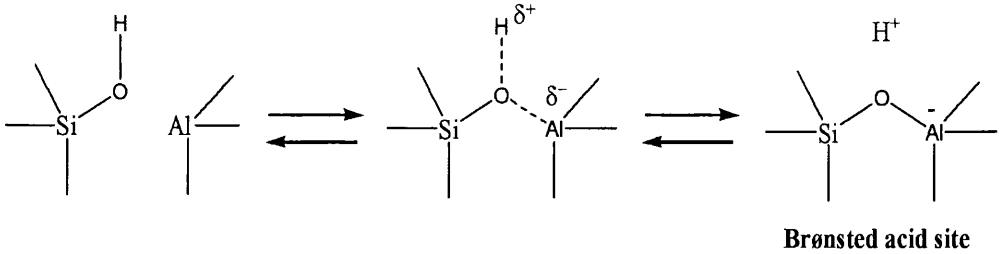

Figure 1.1.14: Brønsted acidity[5]

Lewis acid sites are created when two Brønsted acid sites are dehydroxylated on calcination (**Figure 1.1.15**). During the calcination of the zeolite, water is removed from the porous network as vapour. Consequently, H^+ is removed from the hydroxyl group adjacent to an aluminium centre. Dehydration of a neighbouring acid site (loss of OH^- from silicon) is also observed. This then becomes co-ordinately unsaturated (positively charged) and can accept an electron pair (Lewis acid site). Initially, Lewis acid sites are unstable and oxygen deficient. Therefore, they undergo dealumination generating non-framework alumina with Lewis acidity.

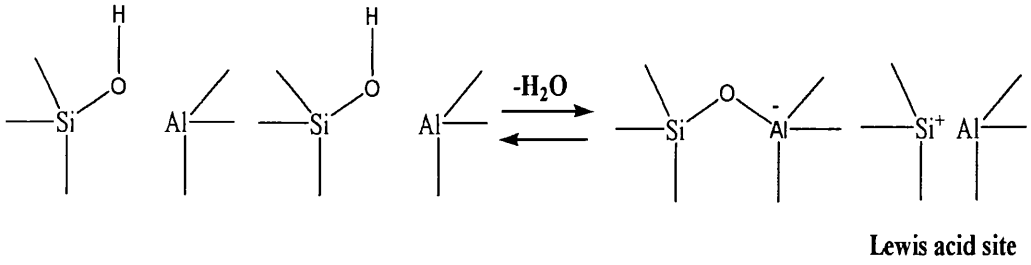

Figure 1.1.15: Lewis acidity[5]

The acid site strength is influenced by the Si/Al ratio and the distribution of aluminium throughout the zeolite framework. It is generally accepted that the higher the Si/Al ratio (i.e. less Al^{3+} ions in the framework) the fewer the number, and stronger the strength of acid sites throughout the framework. Also, the lower the Si/Al ratio (i.e. more Al^{3+} ions in the framework) the grater the number and weaker the strength of acid sites throughout the framework. The framework Si/Al ratio of zeolites can be controlled by dealumination (removal of aluminium) or silicon reinsertion (replacement of aluminium with silicon).

1.1.8.15 Dealumination[5]

Dealumination is the removal of aluminium from the zeolite framework. Dealumination decreases the framework Si/Al ratio, consequently:

1. the cation exchange capability is reduced

2. the total number of acid sites is decreased

3. the mean acid strength is increased

4. the hydrothermal stability is increased

Typically, zeolites are dealuminated by steaming, acid leaching and various chemical treatments (e.g. fluoro compounds and silicon tetrachloride).

1.1.8.16 Cation-exchange capability[5]

Anionic framework sites $[AlO_2]^-$ are created subsequent to the isomorphous substitution of some of the Si^{4+} and Al^{3+} within the zeolite framework. A net negative charge is produced which is balanced by non-framework cations. Charge balancing cations are found within the intracrystalline channels and polyhedral cages of the zeolite framework. The hydrated cations access the zeolite network through 8-T (or larger) apertures, whereas unsolvated cations typically enter the zeolite framework via 6-T ring (or smaller) apertures.

Solvated cations within the zeolite framwork are mobile and can migrate between anionic framework sites. Conversely, unsolvated cations are trapped within the polyhedral cages and experience much slower migration between anionic framework sites. Solvated cations ($\mathbf{M_b}$) from external solutions can enter the zeolite framework through 8-T ring apertures and exchange with the zeolite's original cations ($\mathbf{M_a}$) as illustrated in equation **1.1.1.**

$$M_a^{-}Zeolite(s) + M_b^{+}(aq) \longrightarrow M_b^{-}Zeolite(s) + M_a^{+}(aq)$$

Equation 1.1.1[5]

Cation exchange is reversible, with the degree of exchange depending essentially on the number of cations in the exchange solution and in the zeolite. To achieve complete exchange, repeated treatments with fresh solutions are required.

Ion-exchange can alter the pore sizes of a zeolite. The extent of which is dependant on the size and valency of the cation. This was illustrated previously in zeolite A, where the cations present reduce the mean pore aperture diameter (Section 1.1.x). In addition, the nature and location of the cations within the zeolite framework can affect the catalytic activity and adsorbtion ability of the zeolite.

1.1.8.17 Catalytic properties of zeolites

Zeolites are highly valued catalysts in numerous reactions, due to their unique collective of properties. The high internal surface area and strong acid sites make them potentially active catalysts. The selective sorption, and molecular sieving properties allow them to be shape selective. The selectivity exhibited by zeolite catalysts is categorized into three types:

1. **Reactant selectivity** (*diffusion controlled*)

Size and shape restrictions (1.e.pore and channel dimensions) of the zeolite structure can prevent access to some reagents and facilitate the sorption of others. (illustrated in **Figure 1.1.16**)

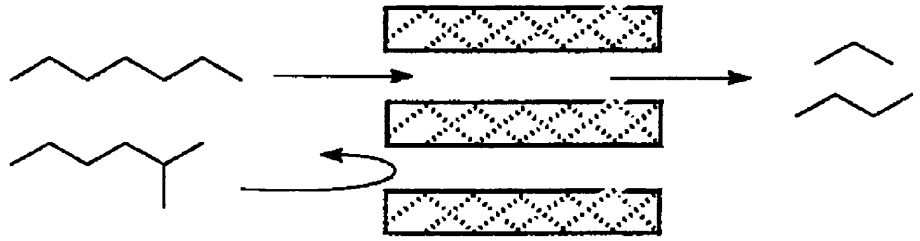

Figure 1.1.16: Schematic representation of reactant selectivity in zeolite catalysis.[5]

2. **Product selectivity:** (*diffusion controlled*)

If several products are formed within the large supercage voids of the zeolite, only products with suitable dimensions will be able to exit the zeolite (due to size restrictions of the channels and apertures). Products that are too large to exit, will be retained within the internal zeolite framework. (Illustrated in **Figure 1.1.17**)

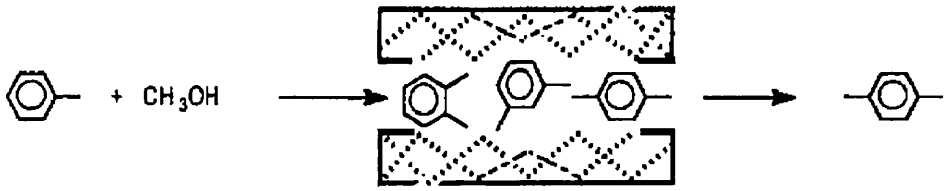

Figure 1.1.17: Schematic representation of product selectivity in zeolite catalysis.[5]

3. **Transition state selectivity:** (Geometrically controlled)

This arises when the zeolite framework restricts the formation of a bulky intermediate product (illustrated in **Figure 1.1.18**).

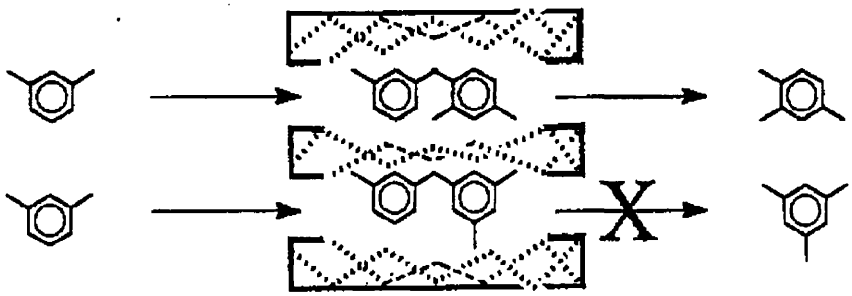

Figure 1.1.18: Schematic representation of transition state selectivity in zeolite catalysis[5]

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Chapter 1, Part 2

The importance and significance of polyethylenenaphthalate (PEN)

1.2.1 Introduction

Considerable attention has been focussed on the use of zeolites in industrially important processes. One such process is the commercial synthesis of 2,6-dimethylnaphthalene (**Figure 1.2.1**), in which solid catalysts are commonly employed. Part 2 of this Chapter introduces 2,6-dimethylnaphthalene and the industrial importance of its application in the production of polyethylenenaphthalate.

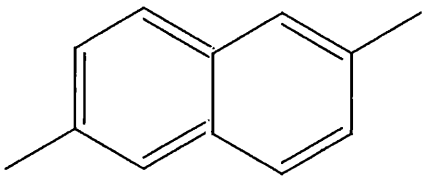


Figure 1.2.1 : 2,6-Dimethylnaphthalene

1.2.2 The importance of 2,6-dimethylnaphthalene

The production of 2,6-dimethylnaphthalene (abbreviated to 2,6-DMN) has sparked a lot of interest within many companies due to its significance in industry, and has been produced for many decades by numerous commercial processes.

The industrial significance of 2,6-DMN stems from its role in the production of 2,6-naphthalenedicarboxylic acid (abbreviated to 2,6-NDA) (**Figure 1.2.2**), where 2,6-DMN is a desirable raw material in this process. The production of 2,6-NDA from 2,6-DMN will be discussed later in more detail.

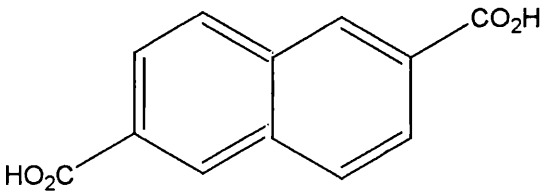


Figure 1.2.2 2,6-Naphthalenedicarboxylic acid

2,6-NDA is a beneficial monomer for the production of high performance polymeric materials and engineering plastics. Examples include polyesters, polyamides and liquid crystal polymers (LCP)[1]. Therefore, 2,6-NDA has great scope as a profitable material and is ultimately valued in the chemical industry.

1.2.3 The use of 2,6-NDA in the manufacture of polyethylenenaphthalate

The manufacture of polyethylenenaphthlate (abbreviated to PEN) (**Figure 1.2.3**) is the most extensive and significant application of 2,6-NDA (20 million tonnes produced per annum). PEN is manufactured commercially by the transesterification (the process of exchanging the alkoxy group of an ester with an alcohol) of either 2,6-naphthalenedicarboxylic acid or dimethyl-2,6-naphthalenedicarboxylate (abbreviated to 2,6-NDC) (**Reaction scheme 1.2.1**)[2].

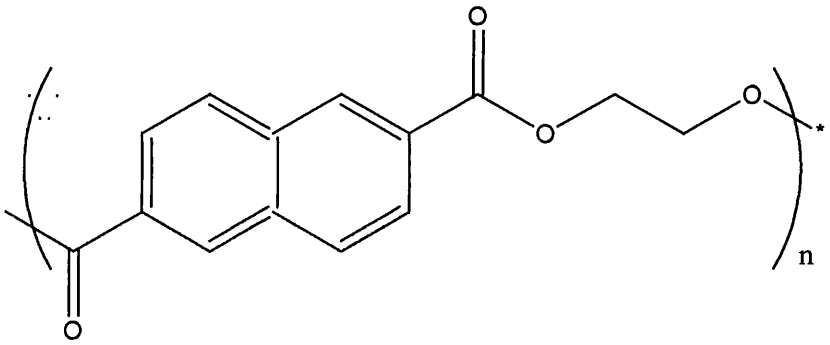
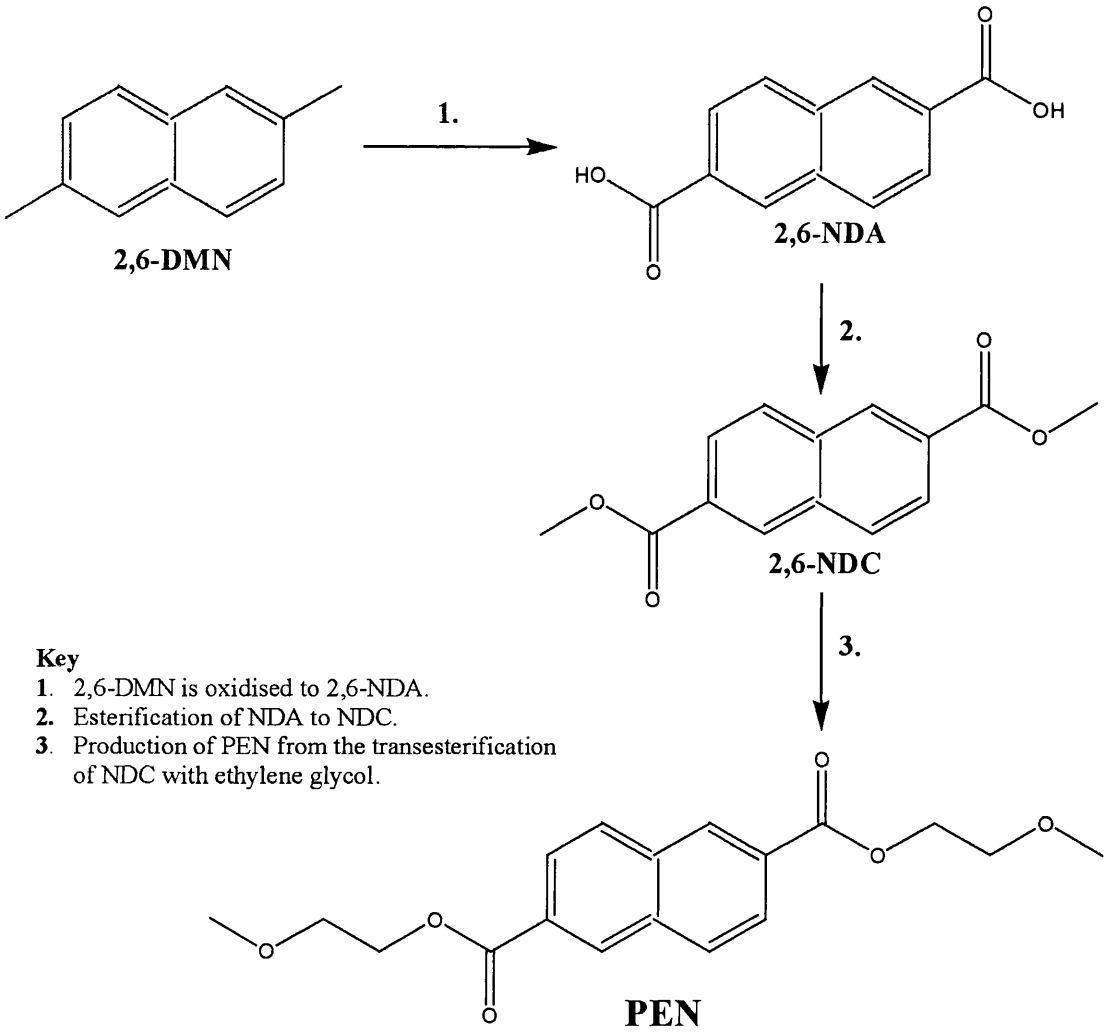


Figure 1.2.3: Polyethylenenaphthalate



Key
1. 2,6-DMN is oxidised to 2,6-NDA.
2. Esterification of NDA to NDC.
3. Production of PEN from the transesterification of NDC with ethylene glycol.

Reaction scheme 1.2.1: Process for the production of PEN from 2,6-DMN

PEN has a variety of advantageous properties as a material which makes it suitable for the applications of a high performance polymer. These include barrier, mechanical, thermal and dielectric properties[1,2]. These properties have ensured that PEN has a high growth potential in the packaging industry[2].

Fibres which are produced from PEN have mechanical, chemical and electrical properties superior to equivalent polyterephalate (**Figure 1.2.4**) fibres[2]. Such properties include, for example, excellent tensile strength and thermal resistance. Tie cords, hoses, belts and electrical insulation are therefore a few of the applications of the industrial high strength fibres produced from PEN[2]. The first world scale 2,6-

NDC plant (60 million lb per year capacity) started up at BP Amoco's Decatur, Alabama site in 1995[2].

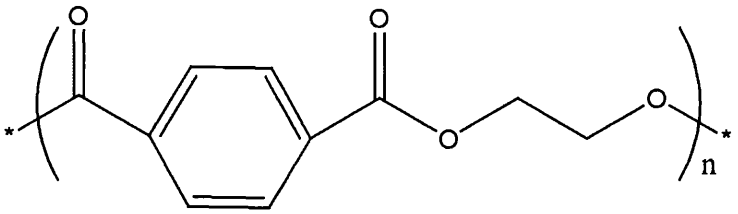


Figure 1.2.4 Poly(ethyleneterephalate)

Films from PEN also have many uses in everyday life, where they are used to manufacture magnetic recording tape and electronic components, applications have great economic significance in industry. Films manufactured from PEN also have a superior resistance to gas diffusion in particular the diffusion of carbon dioxide, oxygen and water vapour. This is very advantageous, allowing films of PEN to be used for the manufacture of "hot fill" type food containers [3]. Furthermore, PEN is a promising material for gas-barrier bottles, especially reusable bottles for beer and other carbonic acid containing beverages, which serve for the reduction of hydrocarbon consumption and waste[3].

1.2.4 Synthesis of 2,6-NDA

The manufacture of high quality PEN required for the aforementioned applications is ensured by the use of essentially pure 2,6-NDA as a starting material. The purified 2,6-naphthalenedicarboxylic acid is commonly synthesised by a heavy metal catalysed oxidation of 2,6-DMN carried out in the liquid phase using molecular oxygen as the source for the oxidation reaction. During this process the methyl substituents on the naphthalene ring of the 2,6-DMN are oxidised, using molecular oxygen, to the corresponding carboxylic acid substituents.

There are many examples of this liquid phase reaction reported in literature[4a-4e]. The U.S.Pat.No. 5,183,933, for example, discloses a process for oxidising 2,6-DMN to 2,6-NDA using a source of molecular oxygen, a solvent comprising an aliphatic monocarboxylic acid, and a catalyst comprising cobalt, manganese and bromine components[4a]. For 2,6-NDA to be produced continuously in high yield with low levels of impurities, the patent states that the contents of the reaction zone must be maintained at a temperature within the range of 370 °C to 420 °C. It also states that the pressure must be sufficient to maintain a portion of the monocarboxylic acid in the liquid phase, thereby oxidising the 2,6-DMN to the desired 2,6-NDA.

1.2.5 Limitations associated with the oxidation process

There is a draw back to the oxidation process owing to the fact that unwanted by-products are produced. Oxidation of one of the rings the of 2,6-DMN molecule produces trimellitic acid (TMLA), which is particularly unfavourable since TMLA complexes to manganese and cobalt and deactivates the oxidation catalysts, making the oxidation process self-deactivating. Also, incomplete oxidation results in the formation of 2-formyl-6-naphoic acid (FNA). Bromination of the naphthalene ring to form bromonaphthalenedicarboxylic acid (BrNDA) can also occur during the oxidation reaction. In addition to these side reactions 2-naphthoic acid (2-NA) is also formed from the loss of one methyl (or carboxylic acid) substituent during the oxidation reaction.

The formation of these aforementioned side products as well as the presence of other unidentified side products are extremely disadvantageous since they serve to greatly contaminate the 2,6-NDA which is being manufactured. 2,6-NDA has a high insolubility in standard solvents such as water and aromatic hydrocarbons, making

purification of 2,6-NDA by a simple purification procedure such as recrystallisation extremely difficult to achieve. Therefore, contamination of 2,6-NDA by various side products and impurities is a major drawback since they are almost impossible to remove unless complex purification techniques are adopted, which can in turn be economically unfavourable. Therefore, clearly it is of great importance to produce 2,6-NDA without the formation of these unwanted side products and impurities.

1.2.6 Decreases in the demand for PEN

There are many factors which have contributed to the decrease in growth of the demand for PEN in industry. The economics for the production of PEN are dependent on the price and availability of the 2,6-NDA monomer which in turn depends on the price of its raw material 2,6-DMN. Consequently, the 2,6-DMN monomer is required to be available in vast quantities, essentially highly pure and of good quality, whilst still ensuring that the process is economically viable.

1.2.7 Isomers of dimethylnaphthalene

As mentioned earlier, one of the applications of 2,6-NDA is a monomer for high performance polymers, which consequently demands that 2,6-NDA is highly pure isomerically, and this in turn requires that the raw material 2,6-DMN is also isomerically pure to a high degree. This can prove to be problematic since 2,6-DMN has 9 isomers (1,2-, 1,3-, 1,4, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, and 2,7-) in addition to the desirable 2,6-isomer (**Figure 1.2.5**). It is therefore of great interest that when 2,6-DMN is produced it is free from of any of the aforementioned isomers other than the desirable 2,6-DMN.

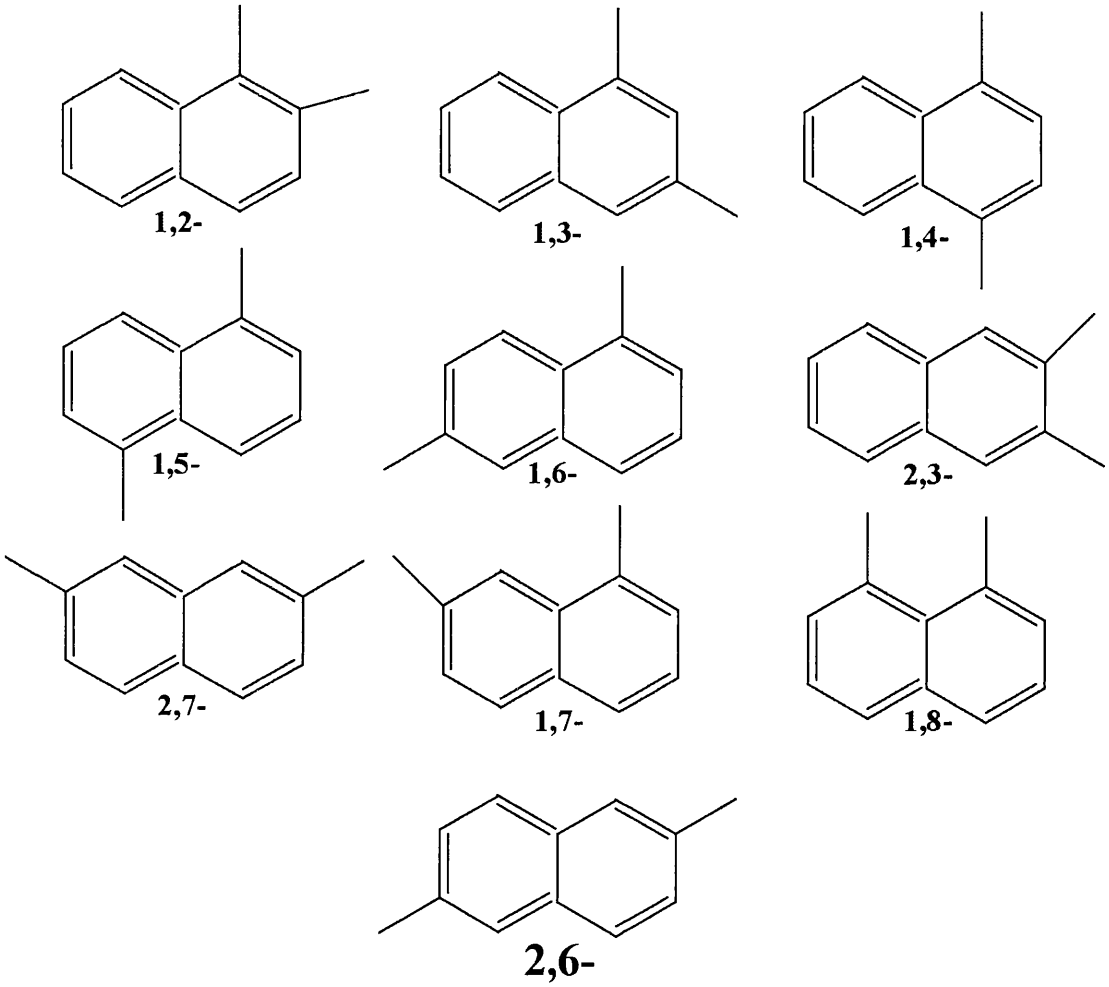


Figure 1.2.5: Isomers of dimethylnaphthalene

The production of 2,6-DMN is an interesting area of research for industrial companies since it has a variety of widespread uses and applications and its synthesis, free of other isomers, at low cost and high purity in vast quantities is consequently of great worth financially.

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Chapter 1, Part 3

Selective synthesis of dialkylnaphthalenes

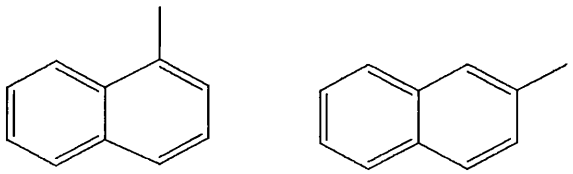
1.3.1 Introduction

As discussed in Part 2 of this Chapter, 2,6-dimethylnaphthalene (2,6-DMN) is a very profitable intermediate in the production of polyethylenenaphthalate (PEN). In view of this, many industrial companies have developed processes for producing highly pure 2,6-DMN, in a high yield. This section of work gives a brief overview of past and present methods for the production dialkylnaphthalenes in industry, concentrating mainly on 2,6-DMN.

1.3.2 Initial methods for producing 2,6-DMN

Petroleum fractions which boil within the range of 400-500 °C contain significant amounts of alkylnaphthalenes. Consequently, the initial methods for producing 2,6-DMN involved isolation of naphthalene from such refinery streams derived from gas and oil. These hydrocarbon charge stocks are obtained in both catalytic and thermal cracking processes, with the aromatic content varying within the range of 25-97 %.

Examples of 2,6-DMN and other isomers of dimethylnaphthalene being produced from cracked petroleum fractions have been reported in the literature[1-3], US Patent 3,153,675 being one such example. In this invention, it is said that the aromatic hydrocarbon charge stock boils within the range of 440-525 °C. The charge stock is composed mainly of alkylnaphthalenes, with the alkyl groups appearing at both the α and β positions on the naphthalene nucleus (**Figure 1.3.1**).



α -Methylnaphthalene **β-Methylnaphthalene**

Figure 1.3.1: Diagram to show α-methylnaphthalene and β-methylnaphthalene

Figure 1.3.2.shows a typical composition of the recycle fraction

Compound	%
beta -Methylnaphthalene	70
alpha -Methylnaphthalene	15
Dimethylnaphthalenes	15

Figure 1.3.2: A typical composition of the recycle fraction

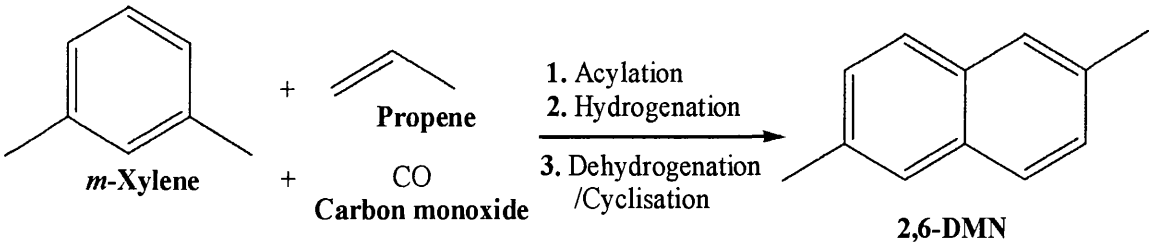
The initial processes for the production of 2,6-DMN from these petroleum fractions carried many limitations. The main limiting factor of this method was the low concentration of 2,6-DMN contained in the charge stocks. This was coupled with the presence of other isomers of dimethylnaphthalene. Therefore, problems with the separation, isolation and the actual purification of the desirable 2,6-DMN were encountered. This method is deemed to be non-cost effective and unpractical due to the limitations observed and the multiple steps employed. Therefore, this process is unsuitable for the inexpensive mass production of 2,6-DMN required for producing PEN.

1.3.3 Current methods for producing 2,6-DMN

In recent years various methods of synthesising 2,6-DMN from different starting materials have been proposed. Essentially, there are 4 main routes for producing 2,6-DMN which have been developed by industrial companies. These include the build up of a naphthalene derivative from two separate units, and the direct alkylation of naphthalene. Each of these routes will be discussed in turn in the following sections.

1.3.4 Route 1: The synthesis of 2,6-DMN from *m*-xylene and propene

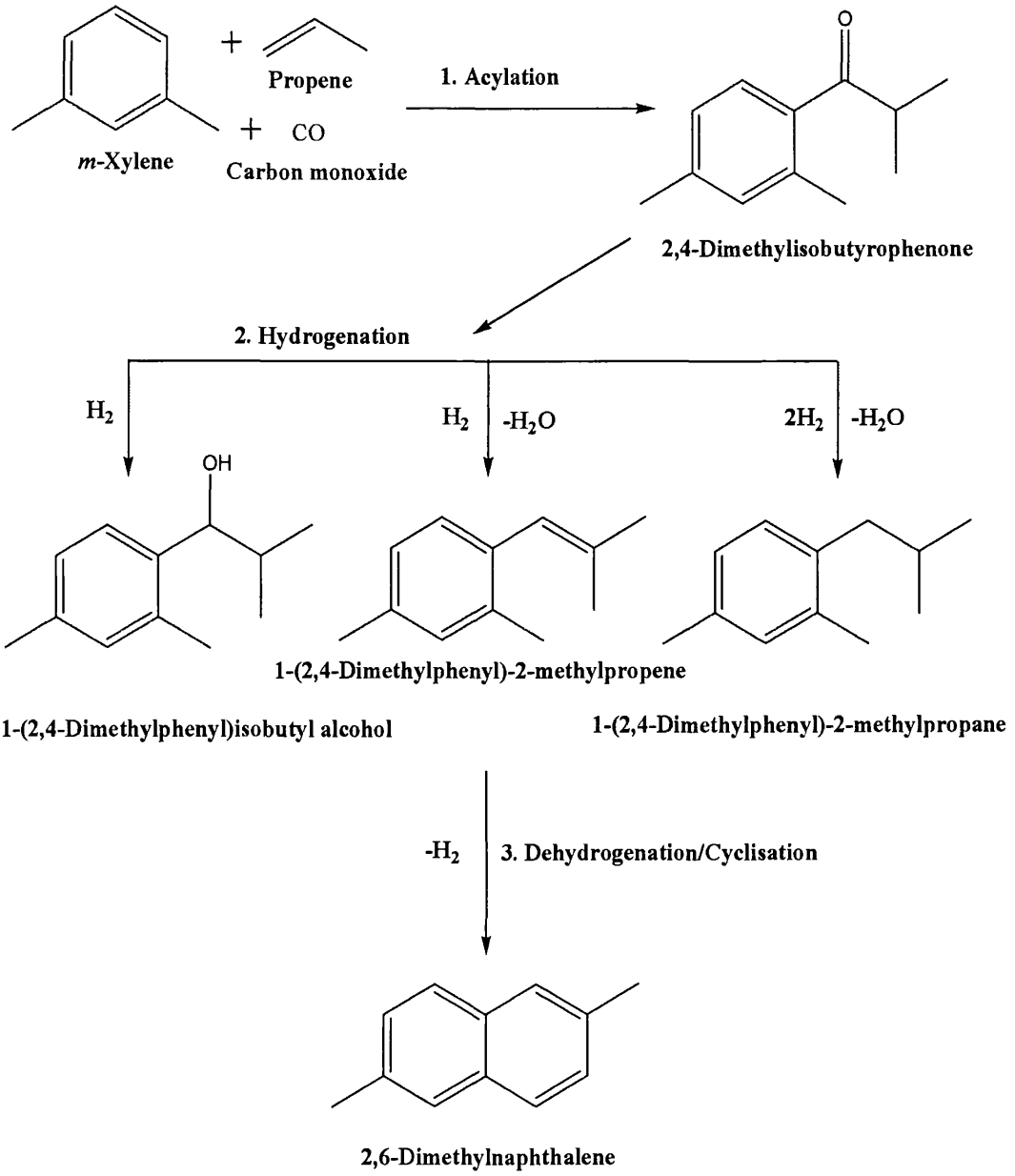
The synthesis of 2,6-DMN from *m*-xylene and propene (**Reaction Scheme 1.3.1)** is proposed by Mitsubishi Gas Chemicals Inc[4,5], and includes three major acid and base catalysed reaction steps (**Reaction Scheme 1.3.2**). This process aims to produce a route for the selective production of 2,6-DMN from inexpensive starting materials.



Reaction Scheme 1.3.1: Synthesis of 2,6-DMN from *m*-xylene and propene proposed by MITSUBISHI GAS CHEM CO INC.

The process disclosed by Mitsubishi is described in US Patent 5,023,390. The first stage of the reaction involves an acylation reaction to synthesise 2,4-dimethylisobutyrophenone.

Predetermined amounts of HCl and $AlCl_3$ (Lewis acid catalyst) were placed in an anticorrosive autoclave, where the temperature was kept within a range of 0-60 °C. Carbon monoxide was introduced under a pressure of 10-80 $kgcm^{-2}$, leading to the formation of 2-chloropropane. *m*-Xylene was then introduced while stirring. A 95 % yield of 2,4-dimethylisobutyrophenone was observed, based on the weight of *m*-xylene[5]. The reaction was completed in a residence time of 15-180 minutes. The Lewis acid catalyst was separated from the product by phase separation.



Reaction Scheme 1.3.2: Three stage process to synthesise 2,6-DMN from *m*-xylene and propene, proposed by MITSUBISHI GAS CHEM CO INC.

The second stage of the reaction involved the hydrogenation of the carbonyl group of 2,4-dimethylisobutyrophenone in a liquid phase. The reaction was carried out in the presence of a Raney type catalyst such as Raney nickel, to produce a mixture of 1-(2,4-dimethylphenyl)isobutyl alcohol, 1-(2,4-dimethylphenyl)-2-methylpropane and 1-(2,4-dimethylphenyl)-2-methylpropene. A 97 % conversion of

2,4-dimethylisobutyrophenone, with a 98 % selectivity towards 1-(2,4-dimethylphenyl)isobutyl alcohol was observed[5].

The preferred hydrogenation product was 1-(2,4-dimethylphenyl)-2-methylpropene, since a small amount of hydrogen was required to produce it. Moreover, when 1-(2,4-dimethylphenyl)-2-methylpropene was subjected to dehydrogenation and cyclisation (third stage), 2,6-DMN was obtained in the highest yield when compared to the reactions with the other hydrogenation products. 1-(2,4-Dimethylphenyl)-2-methylpropene was generated on dehydration of 1-(2,4-dimethylphenyl)isobutyl alcohol by a gas phase reaction catalysed by active alumina or silica-alumina. 100 % conversion of 1-(2,4-dimethylphenyl)isobutyl alcohol was observed, with a 99 % selectivity towards 1-(2,4-dimethylphenyl)-2-methylpropene[5].

The third stage of the reaction involved the dehydrogenation and cyclisation of 1-(2,4-dimethylphenyl)-2-methylpropene, to generate the desired 2,6-dimethylnaphthalene. 1-(2,4-dimethylphenyl)-2-methylpropene was contacted with a metal oxide catalyst such as iron oxide catalyst, at elevated temperatures in the gas phase. A lower conversion was observed in the final dehydrogenation and cyclisation step (89 % conversion of 1-(2,4-dimethylphenyl)-2-methylpropene). A low selectivity towards the desired 2,6-DMN isomer was also observed (62 % selectivity towards 2,6-DMN)[5].

1.3.4.1 Advantages and disadvantages of the Mitsubishi process for synthesising 2,6-DMN

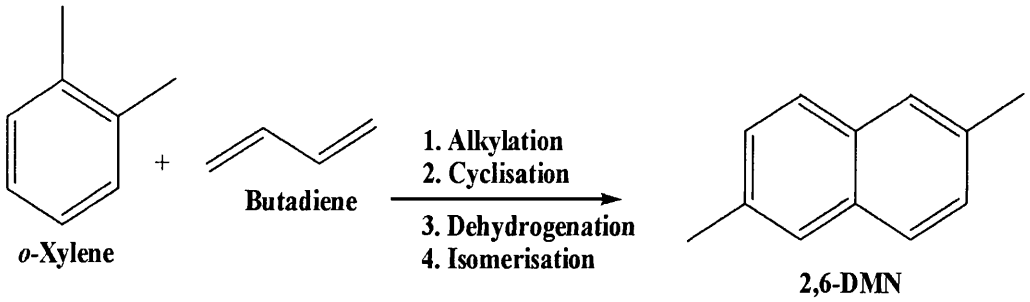
The major plus of this process is associated with the starting materials, which are inexpensive and easily obtainable. This reduces the overall cost of the process making it more economically viable and profitable.

The limitations of the process are associated with the Lewis acid catalyst employed in the acylation step. More than a stoichiometric amount is required and it is non-regenerable. This is due to the formation of a complex between the product and the catalyst, the subsequent hydrolysis of which leads to the loss of the catalyst and the formation of hazardous, corrosive waste products. The disposal of these waste products has immense environmental implications. The Lewis acid catalyst is therefore industrially unfavourable because of its toxicity. The use of zeolites as alternative catalysts in the acylation of aromatic compounds has been well documented and is discussed at length in Chapter 2.

This process is also limited in terms of the dehydrogenation and cyclisation step, with relatively low yields (89 %) and selectivities of 2,6-DMN (62 %) being observed.

1.3.5 Route 2: The Synthesis of 2,6-DMN from *o*-xylene and butadiene

The synthesis of 2,6-DMN from *o*-xylene and butadiene (**Reaction Scheme 1.3.3**) is proposed by BP AMOCO and Mitsibushi Gas Chemicals Inc[4,6-8], and includes four major acid and base catalysed reaction steps (**Reaction Scheme 1.3.4**).



Reaction Scheme 1.3.3 Synthesis of 2,6-DMN from *o*-xylene and butadiene proposed by BP AMOCO.

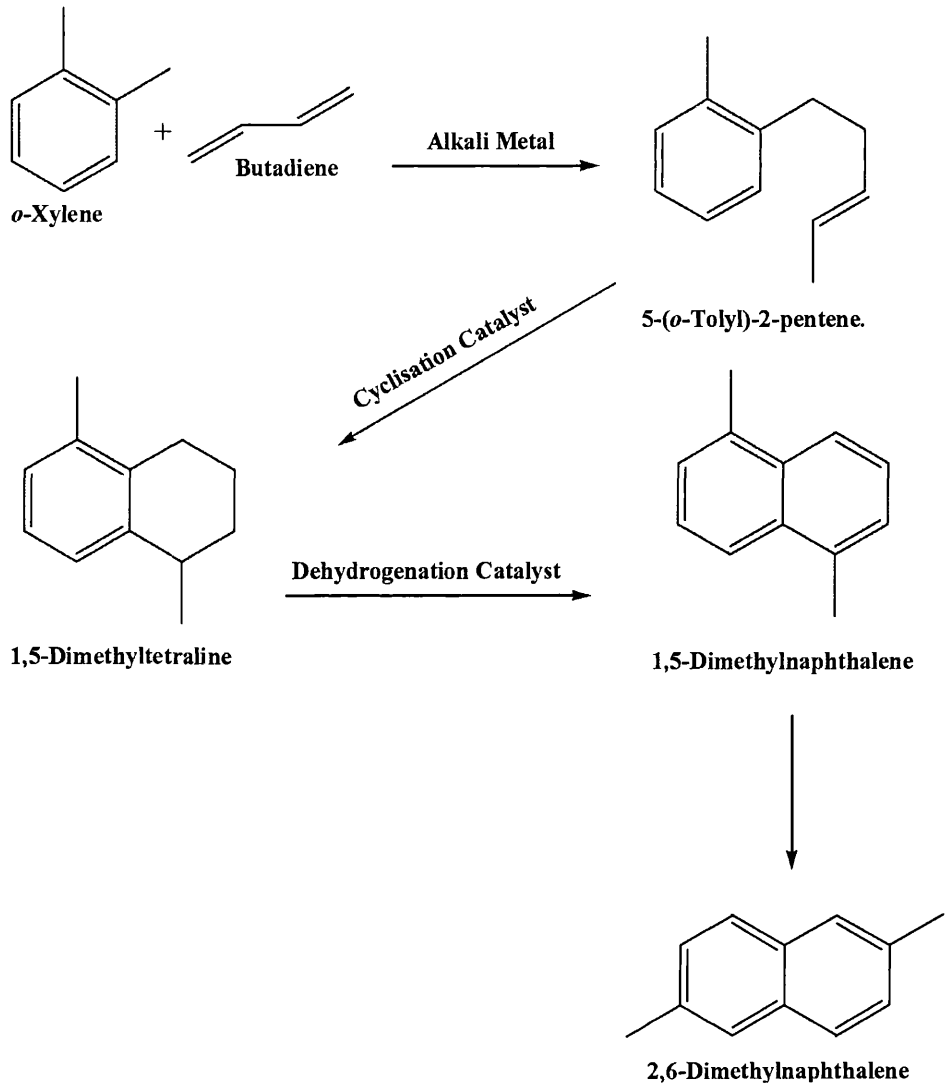
The process is based on the ready availability and low cost of *o*-xylene as a starting material. It aims to provide a route for selectively manufacturing a specific dimethyltetralin isomer in high yield, by the cyclisation of an alkyl benzene. The

dehydrogenation of the aforementioned dimethyltetralin will in turn provide a route for the selective production of 2,6-DMN in high yield.

The first step in this process proceeds via a side chain alkylation of *o*-xylene with butadiene, to generate 5-(*o*-tolyl)-2-pentene. This step is catalysed by a solid superbase, Na/K_2CO_3 at a temperature of 140 °C in a fixed bed reactor. The selectivity based on butadiene was approximately 93% at a 30% conversion of *o*-xylene[8].

The second step of the process involves the acid catalysed cyclisation of 5-(*o*-tolyl)-2-pentene to give 1,5-dimethyltetralin. This step is carried out preferentially in the liquid phase in a slurry reactor at temperatures between 200-450 °C. In the presence of a Cu/Pd doped ultrastable Y-zeolite with hydrogen at 150 °C. A yield of 92-94 % was achieved[8]. The presence of hydrogen is advantageous because it depresses the formation of high boiling C_{24} dimer alkylate by-product.

The third step involves the dehydrogenation of 1,5-dimethyltetralin, to generate 1,5-dimethylnaphthalene. The reaction was carried out in the presence of a noble metal catalyst on alumina, silica or activated carbon. The reaction occurs between temperatures of 220 °C and 420 °C at increased pressure of up to 20 atm (300 psi). At 400 °C and 14 atm, a 99% conversion and 99% selectivity were achieved[8] (The high pressure used is required to keep the feedstock in the liquid phase).



Reaction Scheme 1.3.4: Four stage process to synthesise 2,6-DMN from *o*-xylene and butadiene, proposed by BP AMOCO.

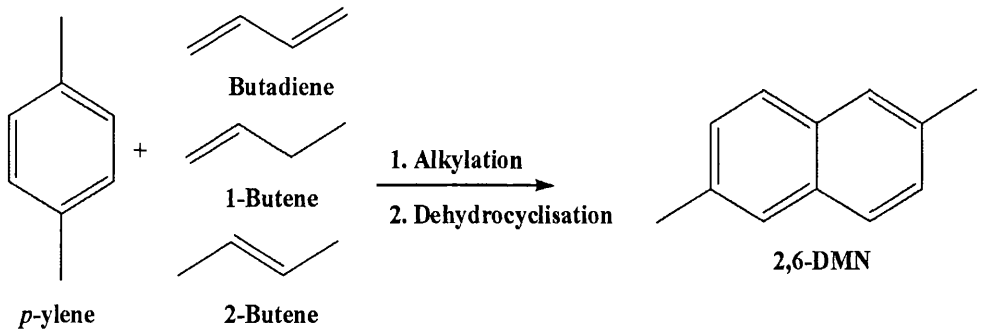
The fourth step involves the isomerisation of 1,5-dimethylnaphthalene to give the desired 2,6-dimethylnaphthalene isomer. In this isomerisation step, acidic dealuminated Y-zeolite or a beta zeolite, having a low Si/Al ratio and low Na content, was employed. The reaction was carried out in a slurry reactor at temperatures ranging from 240-350 °C, with a pressure of up to 5 atm (~75 psi). A 42% yield of the desired 2,6-DMN isomer, and 40 % yield of the 1,6-DMN isomer were obtained[8]. The desired 2,6-isomer was separated by selective adsorption or fractional crystallisation[8].

1.3.5.1 Advantages and disadvantages of the process for producing 2,6-DMN proposed by BP AMOCO

As with the previous route, the starting materials (*o*-xylene and butadiene) are readily available and inexpensive. On the down side, the reaction involves four steps, each of which has a relatively low selectivity and yield. The 2,6-DMN isomer was only obtained in 42 % yield along with 40 % of the 1,6-DMN isomer. The low yields and selectivities from each step, simultaneously contribute to lowering the overall efficiency of the process. In addition, the separation, isolation and purification of 2,6-DMN, make this process uneconomical. Therefore, this process is in need of further development to make it a more efficient industrial process for producing 2,6-DMN.

1.3.6 Route 3: The synthesis of 2,6-DMN from *p*-xylene and butadiene

The synthesis of 2,6-DMN from *p*-xylene and butadiene (**Reaction Scheme 1.3.5)** is proposed by Optatech[4, 9-10], and includes two major acid and base catalysed reaction steps (**Reaction Scheme 1.3.6**).

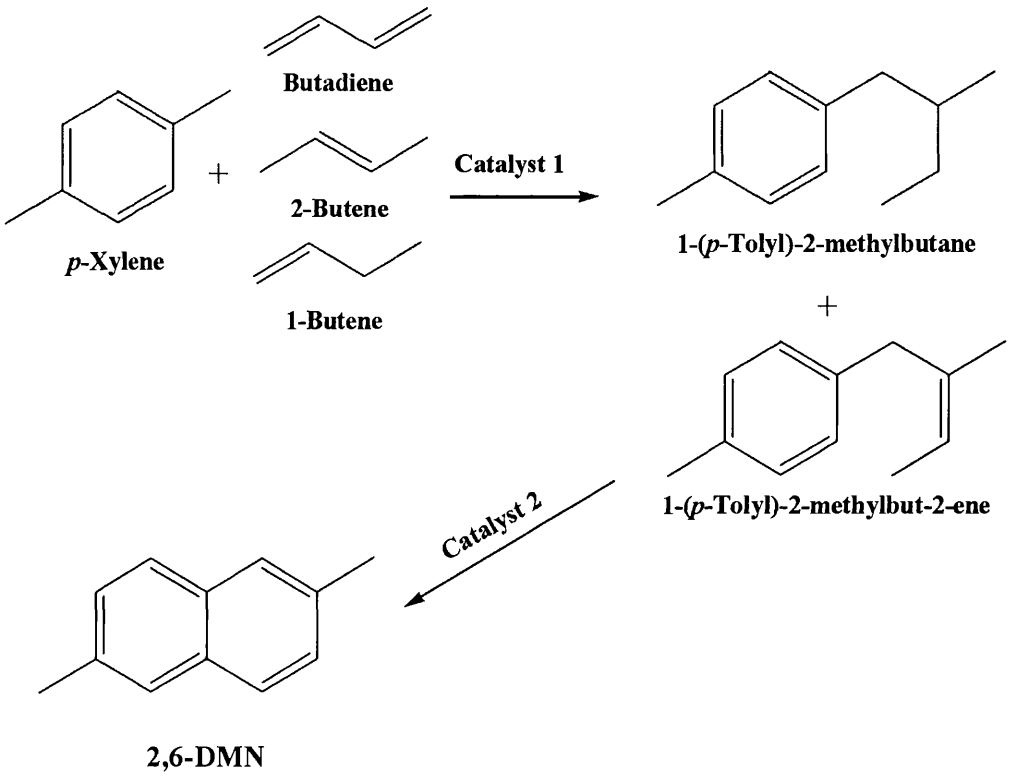


Reaction Scheme 1.3.5: Synthesis of 2,6-DMN from *p*-xylene and butadiene proposed by Optatech.

In the early 1990's the Neste corporation started to develop new technology for the production of 2,6-DMN. Their aim was to improve the production of 2,6-DMN

by reducing investment costs and making it a more economical process. This is achieved by using a two stage process. This is half the number of steps proposed by the aforementioned route by BP AMOCO. They also strive to have high flexibility regarding feed stocks. This is achieved by using *p*-xylene and butadiene as starting materials. *p*-Xylene is very economical as a starting material and has an advantage over *o*-xylene, since it has been at the same level or lower than the spot price of *o*-xylene since October 1997[10].

In 1994, a divestment of the polyolefins and petrochemicals business was undertaken, following the new approach in Neste's strategy. Neste therefore decided to divest in the technology for 2,6-DMN production. In 1995, Optatech corporation purchased the technology from Neste and ever since their interest in the development of the two stage production of 2,6-DMN has continued.



Reaction Scheme 1.3.6: Two stage process to synthesise 2,6-DMN from *p*-xylene and butadiene, proposed by Optatech.

Another reason for using *p*-xylene was to avoid an isomerisation step when generating 2,6-DMN. This cuts down on the cost of the process making it more efficient, profitable and industrially viable.

In the first step of the reaction, *p*-xylene is alkylated with butadiene, to give 4-(p-tolyl)-3-methyl-1-butene. A shape selective basic zeolite catalyst is employed. It was found that the most active catalysts for this purpose were Na dispersed on a zeolite (e.g. NaX and NaY), and Cs dispersed on a zeolite (e.g. CsX and CsY)[10].

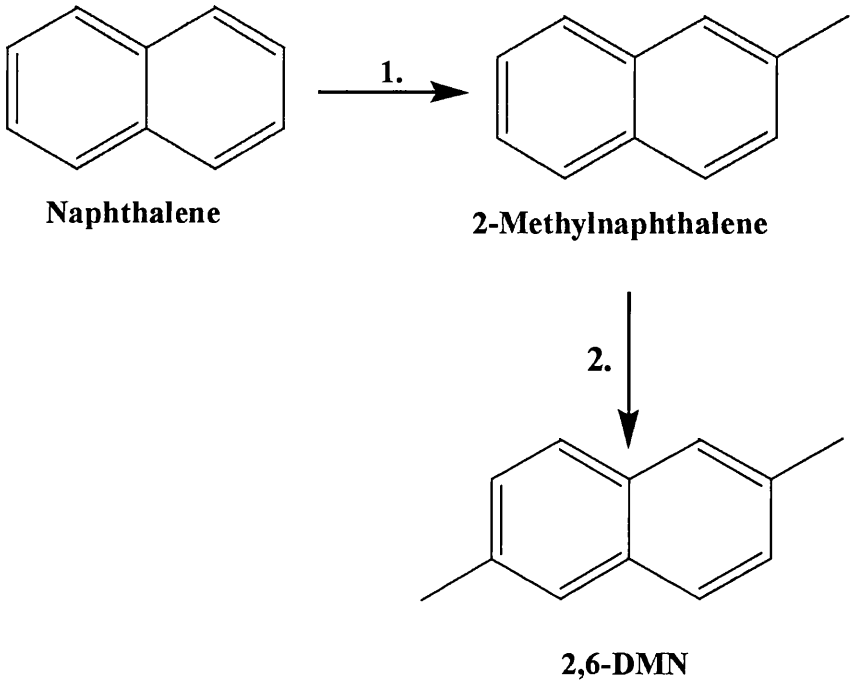
In the second step of the reaction 4-(p-tolyl)-3-methyl-1-butene is dehydrogenated. Subsequent cyclisation generates 2,6-DMN. The dehydrocyclisation reaction is carried out in a tube reactor at 500 °C, over a non-acidic catalyst containing alkali ions. The active catalyst for the dehydrocyclisation reaction was found to be Cr_2O_2 supported on Al_2O_3 and impregnated with K_2CO_3. Lastly, 2,6-DMN is purified by a melt crystalistion process. Conversions between 55 % and 64 % and selectivities between 24 % and 34 % were obtained[10].

1.3.6.1 Advantages and disadvantages of the process for producing 2,6-DMN proposed by Optatech

By using *p*-xylene as the starting material the economics of the process were improved. In addition, an isomerisation step was avoided when generating 2,6-DMN. By reducing the number of steps, the time scale of the process was reduced (compared to routes 1 and 2). This makes the process more efficient and profitable. Despite the flexibility of the feedstock and the absence of the isomerisation step, the process is still limited in terms of the selectivities and yields of 2,6-DMN observed. Conversions between 55 % and 64 %, and selectivities between 24 % and 34 % were observed. These are considerably low. Consequently, this process is probably unfeasible as a profitable industrial chemical process for producing 2,6-DMN.

1.3.7 Route 4: Process for producing 2,6-DMN from the direct alkylation of naphthalene

The synthesis of 2,6-DMN from the direct alkylation of naphthalene has been investigated by amongst others, NKK, Chiyoda and Catalytica, and includes two major reaction steps (**Reaction Scheme 1.3.7**).



Reaction Scheme 1.3.7: Process for producing 2,6-DMN from the direct alkylation of the naphthalene ring.

The first step of the reaction requires methylation at position 2 (β) of the naphthalene ring to give the mono-alkylated product (2-methylnaphthalene). The second stage of the reaction requires the methylation of 2-methylnaphthalene at position 6 (β) of the naphthalene ring, to give the di-alkylated product (2,6-DMN).

The selective alkylation of naphthalene is an extremely desirable but difficult process. In practice, both 1-methylnaphthalene and 2-methylnaphthalene are generated from the initial alkylation step. This increases the number of di-alkylated

isomers that could conceivably be generated in the second alkylation step (**Figure 1.2.5** in Part 2 of this Chapter shows the ten isomers of di-methylnaphthalene).

Figure 1.3.3 illustrates the possible isomers that could be formed from the methylation of 1-methylnaphthalene, 2-methylnaphthalene or from a mixture of 1-methylnaphthalene and 2-methylnaphthalene.

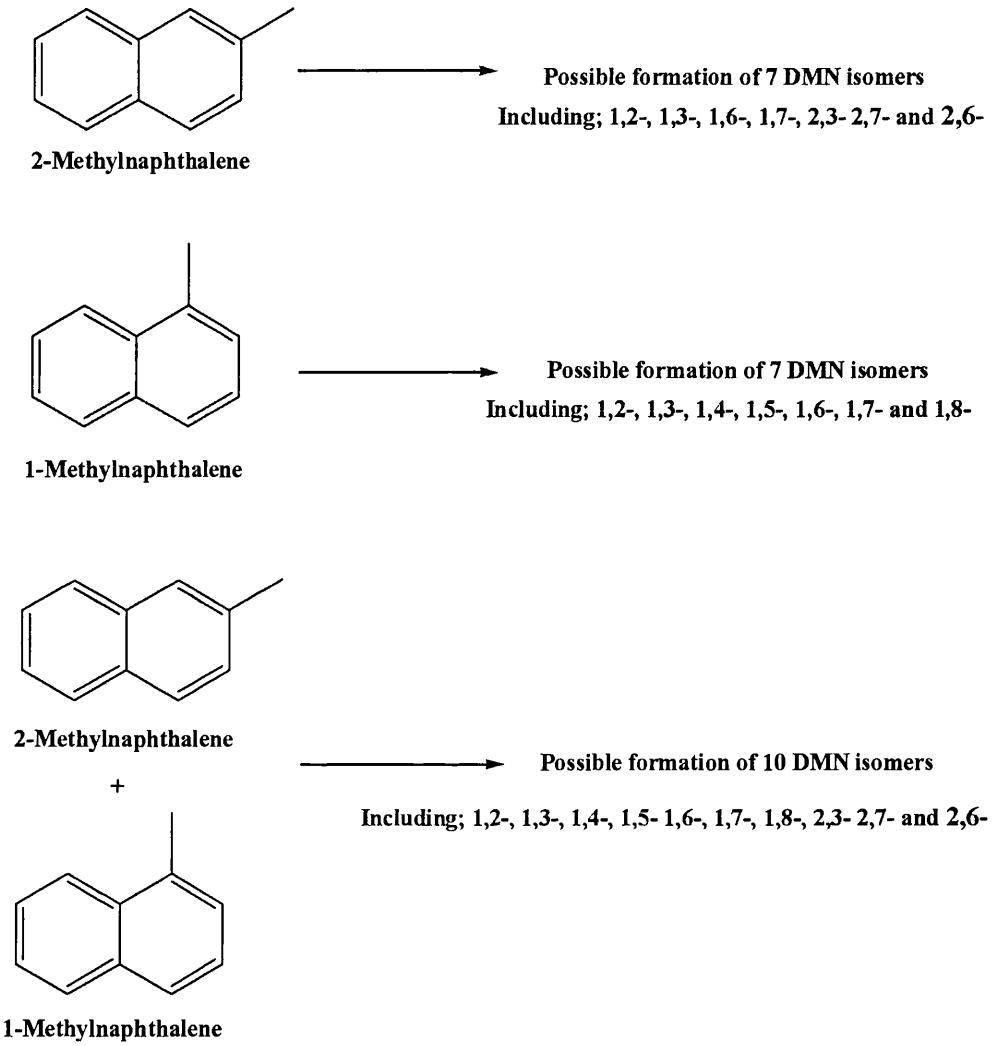


Figure 1.3.3: The possible structure of the di-alkylated product is dependent on the structure of the initial mono-alkylated product.

It can be seen from **Figure 1.3.3** that if 2-methylnaphthalene is solely generated from the initial alkylation of the naphthalene ring, then the desired 2,6-DMN isomer can be formed in addition to six other dimethylnaphthalene isomers. If 1-methylnaphthalene is solely generated from the initial alkylation of the naphthalene ring, the desired 2,6-DMN can not be formed. If a mixture of 1- and 2-methylnaphthalene is generated from the initial alkylation of the naphthalene ring, then all ten possible di-methylnaphthalene isomers can be formed. Therefore, it is essential to achieve an initial β-selective mono-alkylation on the naphthalene ring, so that three di-methylnaphthalene isomers are eliminated (1,4-, 1,5- and 1,8-DMN). It is important to note that this basic rationalization does not take into account the potential for the mono-alkylated products to undergo isomerisation reactions.

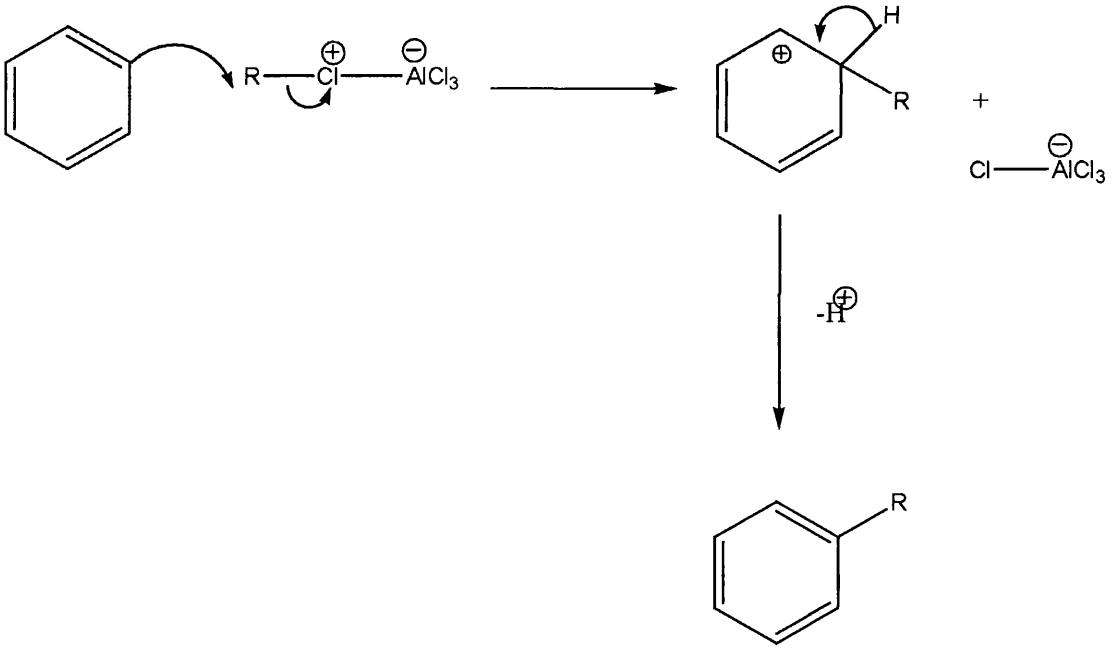
Traditionally, 2,6-DMN was produced by alkylation of naphthalene with an alcohol or an alkene over a Friedel-Crafts type catalyst, such as $AlCL_3$. The next section introduces Friedel-Crafts aromatic alkylation.

1.3.8 Introduction to aromatic alkylation: the Friedel-Crafts reaction

Aromatic alkylation is a very significant reaction in industry and is used extensively. For example more than one million tonnes of ethylbenzene (key intermediate for the synthesis of styrene) is prepared from the reaction of benzene and ethene every year[6]. The Friedel-Crafts aromatic alkylation reaction gets its name after two chemists, a Frenchman called Charles Friedel and an American called James Crafts. They discovered this invaluable reaction in 1877, where it was found that amylbenzene was generated in the reaction of benzene with amyl chloride (1-chloropentane) in the presence of aluminium chloride. The reaction has been widely studied since its discovery and has therefore been the subject of comprehensive reviews[11,12].

The most frequently used alkylating agents include alkyl halides, alkenes, and alcohols. Aluminium chloride is the most frequently used Friedel-Crafts catalyst, but other Lewis acids (e.g. $ZnCl_2$) and proton acids (e.g. H_2SO_4) have also been employed. Although $AlCl_3$ is reported to be the most active metal halide catalyst, the relative activities also depend on a number of other factors, including the nature of the alkylating agent.

Friedel-Crafts alkylation is a net carbon-carbon bond-forming reaction. **Reaction Scheme 1.3.8** illustrates the reaction mechanism when an alkyl halide is reacted with an aromatic compound in the presence of aluminium chloride.



Reaction Scheme 1.3.8: Reaction mechanism for Friedel-Crafts aromatic alkylation of benzene with an alkyl halide.

The complexation of $AlCl_3$ with the chlorine atom of the alkyl chloride weakens the carbon-chlorine bond. This induces charge separation. Reaction of the complex of R-Cl and $AlCl_3$ with benzene produces an arenium ion. Subsequent loss of a proton yields the alkylbenzene product.

1.3.9 Limitations associated with Friedel-Crafts catalysts

The Friedel-Crafts alkylation reactions mediated by Lewis acid catalysts such as aluminium chloride are limited. More than a stoichiometric amount of catalyst is required (by-product conjugate acid (HCl) can fail to dissociate from the Lewis acid centre). Limitations are also associated with corrosion due to the presence of the acid by-product. The presence of aluminium and acid waste steams also gives rise to problems with toxicity handling. The Lewis acid catalysts themselves are difficult to handle, since they are readily hydrolysed by water. Plant corrosion and the safe disposal of the toxic effluent contribute to increasing the overall cost of the process.

In addition, polyalkylation reactions often occur so the reaction is not very selective. This is due to the fact that alkylbenzenes are soluble in the catalyst layer where the reaction occurs. The alkyl substituent also activates benzene towards further reaction.

1.3.10 Heterogenous catalysts in Friedel-Crafts alkylation reactions

Due to the limitations associated with Lewis acid catalysts, a lot of attention has been focussed on the use of heterogenous catalysts such as zeolites and clays in the Friedel-Crafts type alkylation reactions. Solid catalysts are generally more selective, regenerable, reusable, non-corrosive and environmentally benign[13].

Lazslo and Mathy have reported on the synthesis and reactivity of a series of ion-exchanged montmorillonites (K10) in the alkylation of aromatics. Benzene and toluene were generally the substrate and solvent) and alkyl halides, alcohols and alkenes were employed as the alkylating agents[14,15]. In the test reaction with alkyl halides (with benzene and benzyl chloride), the relative activities of the various exchanged cations were significantly different from those of the corresponding Lewis

acid chloride derivatives. This was illustrated by the Al (III) exchanged clay which was one of the least active ion-exchanged clays. 84 % Conversion of benzyl chloride was observed after 9 h[14]. Conversely, Zn(II) exchanged clay was one of the most active ion-exchanged clays, with a 100 % conversion of benzyl chloride being observed after 1.5 h[14]. The opposite is true of homogenous systems. $AlCl_3$ is one of the most powerful Lewis acids, and $ZnCl_2$ one of the weakest. The most active catalyst was found to be the Fe(III) exchanged clay. It was reported that the catalyst could be reused up to five times without significant loss in activity, although further uses required the reaction to be carried out for longer reaction times. The most monoselective catalyst was reported to be the Ti(IV) exchanged clay, with a 77 % monoselectivity being observed (compared to an average 66 % monoselectivity being observed for the other exchanged clays).

Clark *et al.* reported that their clayzic catalyst (formed by supporting $ZnCl_2$ on K10) displays activity several orders of magnitude higher than ion-exchanged materials, in the reaction of benzene with benzyl chloride. 100 % Benzyl chloride conversion was observed with >80 % monoselectivity[15-16]. The considerable activity of clayzic is attributed to the presence of high concentrations of zinc ions in mesopores. The mesopores are created by the acid treatment of the clay. Even though clayzic is commercially available (Environcat EPZ10) and offers many advantages over $AlCl_3$, currently its widespread use is still limited.

In the literature, numerous examples are reported of the successful use of zeolites in aromatic alkylation[6, 13, 17]. Probably one of the most commercially important applications has been the gas phase alkylation of benzene to produce ethylbenzene over ZSM-5 zeolite. Ethyl benzene is synthesised from benzene and ethene (Mobil-badger process), and is a key intermediate in the manufacture of

styrene (one of the most important industrial monomers). The most attractive aspect of zeolite catalysts is their shape selectivity (discussed in Part 1 of this Chapter). This is exhibited in the methylation of toluene with methanol over ZSM-5, with *p*-xylene being the major monoalkylated product observed [17].

Other solid catalysts have been employed in aromatic alkylation, including phosphoric acid-supported on silica. This reaction is used in a well known industrial process for synthesising cumene from benzene and propene[13]. Cumene is the intermediate for the production of phenol and acetone. Its worldwide capacity is around 8 million tonnes per year, distributed over around 40 plants[13].

1.3.11 Alkylation of naphthalene over solid acid catalysts

In an attempt to improve the selectivity of the reaction towards the desired 2,6-dimethylnaphthalene isomer, the use of solid catalysts (especially zeolites, which are highly shape selective) in the alkylation of naphthalene has been investigated extensively.

The routes beginning with naphthalenic compounds would appear to have an economic advantage, because reaction steps are saved not building up the naphthalene ring[4]. The routes described in this section starting with naphthalenics are based on pure feed stocks or refinery streams containing naphthalene compounds.

1.3.12 Methylation of naphthalene[18-27]

Kutz and Corson first demonstrated that benzene, toluene and naphthalene could undergo gas phase methylation over solid catalysts[18]. Methyl chloride and methyl bromide were employed as the methylating agents. Alumina, alumina-silica, activated clay, and aluminium chloride adsorbed on activated carbon, were employed as catalysts.

Fraenkel *et al.* have studied the gas phase methylation of naphthalene over zeolites H-ZSM-5, HM and HY[19]. In the reaction with H-ZSM-5, the 2/1 ratio of the monomethylated product was approximately 8. This indicated a strong β-directing effect. A 2/1 ratio of ~2 was observed with HM and HY. The high β-selectivity exhibited by H-ZSM-5 was also illustrated in the dimethylnaphthalene isomer composition. 2,6- and 2,7-dimethylnaphthalenes (β,β-products) constituted 80 % of the DMN mixture[19]. This was compared to 32-35 % composition of 2,6-DMN in the case of HM and HY. Fraenkel and co-workers also investigated the methylation of 2-methylnaphthalene with H-ZSM-5. Dimethylnaphthalene was the major product observed, and a considerable 83.5 % β,β-selectivity was achieved. When HM was employed, a 37.2 % β,β-selectivity was obtained. It was reported that 1-methylnaphthalene was the major product (formed by isomerisation of 2-methylnaphthalene).

It was thought that over larger pore zeolites (HY and HM), a poor selectivity was obtained since all methylnaphthalene isomers produced are sufficiently small to diffuse away easily. This explains the poor β-, and β,β-selectivity achieved over HM and HY. The higher β- and β,β-selectivity observed with the smaller pore H-ZSM-5 zeolite was attributed to a molecular sieving effect. (since β- and β,β-isomers have the smaller molecular diameters)[19].

In an attempt to increase selectivity towards the desired 2,6-dimethylnaphthalene isomer, Inui and co-workers have modified H-ZSM-5 zeolite by selective neutralisation of the acid sites of the external surface of the catalyst[22]. In the methylation of methylnaphthalene with methanol, the modified H-ZSM-5 zeolite exhibited a longer catalyst life, and higher selectivities to β,β-dimethylnaphthalenes (although not the 2,6-selectivity).

Pu *et al.* have reported that isomorphous substitution of iron and zinc for aluminium in ZSM-5, resulted in an improved selectivity to 2,6-dimethylnaphthalene[23].

Park *et al.* have investigated the methylation of naphthalene with methanol over large pore zeolites such as beta, mordenite and ZSM-12[24]. H-beta was found to be the most active catalyst, with a 99 % conversion being observed. HM and H-ZSM-12 gave conversions of 42.5 % and 51.9 %, respectively[24]. Comparatively high selectivity for methylnaphthalene was observed with HM and H-ZSM-12, with a 72.3 % and 80.4 % selectivity to 2-methylnaphthalene being observed. In addition, H-ZSM-12 was found to be the most selective for dimethylnaphthalene, with a 55.4 % selectivity for 2,6- and 2,7-dimethylnaphthalene being observed[24]. 34.5 % selectivity for 2,6- and 2,7-DMN was observed with Hbeta.

More recently, Tstsui and co-workers investigated how the shape-selective methylation of 2-methylnaphthalene with ZSM-5 should be performed to obtain high conversion[25]. The methylation was conducted in a fixed bed under steady state conditions. The effect of reaction parameters on methylation performance was then investigated. It was reported that an increased conversion was obtained without losing selectivity, by a new unsteady-state reaction method, when compared to the conventional steady-state reaction. This involved adsorption at low temperature and subsequent flush at elevated temperature (LTAF: Low Temperature Adsorption and Flush method).

From an industrial view point, there are two key processes which have developed the methylation of naphthalene. In 1992 a Teijin patent application described a process for the two-step methylation of naphthalene[26]. Firstly, naphthalene is reacted with an isomeric DMN mixture to produce methylnaphthalenes

(MN). Simultaneously, DMN isomers are isomerised over the catalyst to increase the ratio of 2,6-DMN/2,7-DMN in the product. Subsequently, methanol methylation of the MN product from the first step generates a 2,6-DMN enriched product. Both reaction steps involve zeolite catalysts. This process is limited in terms of the low yields being reported for the individual reaction steps. Substantial recycling is also required, which increases the overall cost of the process.

More recently, Mobil technology company and Kobe Steel announced that they were collaborating to develop a new process for producing 2,6-DMN [27]. The new process combines Mobil's synthesis technology (based on the use of MCM-22 large pore zeolite) and Kobe's separation technology. Good results were reported when 2-MN was used as a single feedstock (2,6-/2,7-DMN ratio was 2.3 in the product). However, when a mixture of 1-MN and 2-MN was fed, the selectivity towards the 2,6-DMN isomer decreased (2,6-/2,7-DMN ratio was 1.2-1.5). This is very limiting, as 2,6-DMN and 2,7-DMN isomers are extremely difficult to separate (the difference between their boiling points is 0.3 °C).

In summary, β-selectivity could be achieved over zeolite H-ZSM-5, although, a poor yield of 2,6-DMN was obtained. Non-selective alkylation was seen over large pore HM and HY zeolites.

1.3.13 Isopropylation of naphthalene[4,24-54]

The alkylation of naphthalene with bulkier alkykating agents has been widely investigated. This is because it is easier to stereoselectively differentiate the desired 2,6-isomer from the 2,7-isomer. For example, the isopropylation of naphthalene has been reported extensively in the literature[4,28-54]. Compared with 2,6-di-*tert*-butylnaphthalene and 2,6-dicyclohexylnaphthalene, 2,6-DIPN is automatically more economical in the oxidation process in the production of PEN.

This is because the greater the number of carbon atoms in the alkylating agent, the higher the waste of carbon atoms when the alkyl groups are oxidised to the carboxyl groups.

One of the first groups to report on the isopropylation of naphthalene in the literature was Katayama and co-workers. They found that a high β,β-selectivity as well as 2,6-selectivity could be achieved in the iso-propylation of naphthalene with propene or propan-2-ol[28]. Initially, no reaction was observed with ZSM-5. It was thought the zeolite pores were too small to facilitate the isopropylation reaction. HL and HY zeolites (large pore zeolites) were also employed. The alkylation reaction did proceed, although β,β-selectivities were low (13.9 % for HL). In addition, selectivity for the formation of 2,6-di-isopropylnaphthalene (DIPN) over the 2,7-isomer was not observed for either zeolite (2,6-/2,7 ratio of ~1 being observed).

A high β,β-selectivity (~75 %) was observed when HM was employed and a 2,6-/2,7 ratio of 2 was also observed. The improved selectivity observed with HM was thought to be due to the shape-selectivity of the zeolite. This suggests that the isopropylating agent cannot attack at the α-positions of the naphthalene ring as the zeolite pores are too tight. This size effect was not though to be responsible for the fact that twice as much of the 2,6-isomer was formed over the 2,7-isomer, both isomers having very similar molecular sizes (the dimensions for the 2,6-isomer and 2,7-isomer were reported to be 6.5 x 13.2 Å and 6.5 x 12.5 Å, respectively). It was suggested that the more linear structure of the 2,6-isomer was more able to move in the small one-dimensional tunnels of HM, compared to the 2,7-isomer. It was also reported that HY was more active than HM, with 96.1 % and 68.3 % conversion being observed, respectively. This was explained in terms of the slower diffusion of the reactants and products in the one-dimensional straight channel structure of HM in

comparison to the three-dimensional channels of HY. Moreau *et al.* and Fellmann *et al.* reported similar results on the selective *iso*-propylation of naphthalene over HM and HY zeolites, around the same time[29,30].

Since these original reports set out in the literature in the early nineties, there have been numerous publications regarding the iso-propylation of naphthalene in both the open literature and the patent literature. The idea that HM is selective towards the desired 2,6-isomer, and larger pore zeolites (e.g. HY, Hβ and HL) are normally more active, is generally accepted.

Schmitz and Song have reported that increasing the Si/Al ratio of HM (by dealumination) from 14 to 38 and 74 increased the yield of β,β-DIPN (*ca.* 13 %, 15 % and 20 %, respectively[31]). This was explained on the basis of two observations. Firstly, dealumination causes a small contraction of the HM micropore diameter (XRD analysis of the catalyst). Therefore, it was thought that differences in the diffusion rates of the 2,6-isomer and 2,7-isomer would be magnified. Secondly, it was found that the reactivity of DIPN was significantly reduced when dealuminated zeoltes were employed.

The effects of HM dealumination with regard to coke deposition have been studied by Kim et al.[32-33]. It was found that in non-dealuminated catalysts the formation of coke was faster, when compared to the dealuminated zeolites (coke formation was suppressed). It was thought that coke deposition occurs at the pore entrances in HM zeolites that have a low Si/Al ratio, thus inhibiting the reaction within the pores. Therefore, the lower selectivity for 2,6-DIPN, was due to the relative increase in non-selective catalysis at the external acid sites, which remain active despite coke deposition.

The alkylation of naphthalene in the absence of organic solvent is of interest as it reduces the load downstream. Mathew *et al.* have investigated the *iso*-propylation of naphthalene with *iso*-propanol over several zeolites (HY, HM, Hβ, H-ZSM-5 and H-MCM-22), in the absence of an organic solvent[34]. The highest naphthalene conversion was observed when Hβ was employed (63.4 %). This was attributed to the 3-D channel system made up of twelve membered rings, which allows rapid diffusion of reactant and product mixtures. The lowest naphthalene conversions were observed with H-ZSM-5 and HMCM-22 (3.8 % and 5.3 %, respectively). This was thought to be due to the small pore sizes of the zeolites. HM was found to be the most selective towards the desired 2,6-isomer, with a 2,6-/2,7- ratio of 3.26 being observed. The lowest 2,6-/2,7- ratios were observed with H-ZSM-5 and HMCM-22 (<0.5). This was thought to be due to the absence of shape selectivity, since the reactions occur mostly at the external surface. Interestingly, when dealuminated HM was employed (with Si/Al ratios ranging from 22.5 to 31.8), there was no significant change in selectivity towards the favoured 2,6-isomer.

All these reactions were carried out in the absence of an organic solvent, under nitrogen. To investigate the influence of solvent, reactions were carried out (over HM) with cyclohexane and in the absence of solvent or gas[34]. It was shown that a higher conversion of naphthalene was observed when the reaction was carried out in the presence of N_2, when compared to the neat reaction (with only *iso*-propanol and naphthalene), or when cyclohexane was employed as the medium.

More recently, Lee *et al.* have reported on the activity, selectivity, and stability of a series of dealuminated HM catalysts for naphthalene *iso*-propylation[35]. Reactions were carried out in a high pressure fixed-bed flow reactor. It was found that the stability and selectivity of the dealuminated HM zeolites were significantly

improved, when compared with unmodified HM. For example, in the reaction with the untreated HM (Si/Al 25), a 9.7 % mol conversion was observed. A 2/1 ratio of 1.6 and a 2,6-/2,7-ratio of 1.6 were achieved. In the reaction with dealuminated HM (Si/Al of 72), a 37.3 % mol conversion, a 2/1 ratio of 2.7 and a 2,6/2,7- ratio of 4.1 were achieved. It was noted that poly-*iso*-propylnaphthalenes were not observed in any of the reactions. It was thought that this was due to the small pores of mordenite, which could restrict its formation.

It was reported that all the catalysts employed in the reactions were deactivated to some extent during the reaction. The untreated HM zeolite exhibited the highest degree of deactivation (as well as the lowest conversion compared to the dealuminated zeolites). It was postulated that the activity of untreated HM did not correspond to its high acidity, and that the activity of a solid acid catalyst for this type of reaction was largely influenced by its porosity rather than its acidity [36], although, the formation of coke is supposed to be accelerated by the high acidity of a catalyst.

Therefore, the deactivation of untreated HM was thought to be due to coke formation at the major channel mouth. Thus, access for reactants to the internal channel sites would be restricted. Dealumination of HM reduces the number of acid sites and modifies the pore distribution (resulting in an increase in mesopores). This offers an explanation for the slow deactivation of the dealuminated HM catalysts, which have a lower acid density than the untreated zeolite. In addition, the increased mesoporosity allows more reactants into the zeolite pores and facilitates the products desorbing out of the pores. This is probably why a higher conversion was observed for the dealuminated HM zeolites, compared to the untreated HM zeolite.

With regards to the patent literature, Catalytica have done much work in the *iso*-propylation of naphthalene[38-40]. They describe a two-step process involving the

isomerisation of di-*iso*-propylnaphthalene isomers over a silica-alumina catalyst, and the selective di-*iso*-propylation of naphthalene using HM as the shape selective zeolite.

1.3.14 The cyclohexylation of naphthalene[55-58]

The major problem with the *iso*-propylation of naphthalene is the separation of the desired 2,6-isomer from the product mixture. This is especially true for separation from the 2,7-isomer, since it has a very similar boiling point to the 2,6-isomer. In the cyclohexylation of naphthalene this problem is overcome, with the 2,6-isomer being isolated from the crude mixture by crystallisation[55-56].

Moreau and co-workers have investigated the zeolite catalysed cyclohexylation of naphthalene[57]. The liquid cyclohexylations of naphthalene with cyclohexyl bromide and cyclohexene over HM and HY zeolites were investigated. A low activity was observed with HM, with a 6 % conversion being observed (probably due to the reaction not being able to proceed within the pores of the zeolite). The conversion increased significantly when large pore HY was employed (94 % conversion after only 10 minutes at 200 °C). A 43 % yield of di-cyclohexylnaphthalene (DCN) was achieved[57]. It was found that β,β-selectivity was achieved (79 %), although 2,6-selectivity was not. In the reaction with HY and cyclohexene as alkylating agent, dimerisation of the alkene was observed. This was overcome when the alkene was drip fed into the reaction mixture. Very similar results were observed to the reaction with cyclohexyl bromide over HY. For example the β,β-selectivity was 77 % and the 2,6-/2,7-ratio was 1.2.

More recently, Smith and Roberts investigated the cyclohexylation of naphthalene[58]. Cyclohexene, cyclohexanol and cyclohexyl bromide were employed as the alkylating agents and HY, Hβ, HM, H-ZSM-5 zeolites and MMS (synthesised

mesoporous molecular sieve) were employed. It was reported that all three cyclohexylation reagents achieved similar conversions (*ca.* 95 % naphthalene conversion). However cyclohexanol was less β,β-selective than cyclohexene and cyclohexyl bromide. HY was found to be the most active zeolite, with a 96 % conversion being observed. The least active zeolites were HM and H-ZSM-5, where no reaction took place. An 18 % conversion was observed with Hβ, with a 2 % yield of di-cyclohexlnaphthalenes, although 2,6-selectivity was not achieved, with a 2,6/2,7- ratio of 1.0 being observed[58].

In conclusion, the main advantage of cyclohexylation over *iso*-propylation is the easy separation of the desired 2,6-isomer from the crude product by crystallisation.

1.3.15 The *tert*-butylation of naphthalene[59-66]

There are several studies of the *tert*-butylation of naphthalene reported in the literature[59-66]. For example, Moreau and co-workers investigated the *tert*-butylation of naphthalene with *tert*-butanol as alkylating agent over HY zeolite[59]. It was found that 2,6-di-*tert*-butylnaphthalene (2,6-DTBN) could be easily separated from the crude product by crystallisation. In addition, a high β,β-selectivity was observed, as well as a high selectivity towards the favoured 2,6-DTBN isomer. This is very attractive, where the 2,6-selectivity observed in the *iso*-propylation of naphthalene can be combined with the easy separation of the product observed in the cyclohexylation.

Kulkarni and co-workers have studied the vapour phase *tert*-butylation of naphthalene with *tert*-butanol over modified zeolites[60]. The cerium modified Y zeolite (CeY) was found to be the most selective catalyst, with a 2,6-/2,7-ratio of 1.8 being observed. The highest conversion was observed with HY (74 %). This was probably due to the large pore size of the zeolite.

The *tert*-butylation of naphthalene has also been studied extensively by Smith and Roberts [58, 61]. The *tert*-butylation of naphthalene with *tert*-butanol as alkylating agent and cyclohexane as solvent was conducted over several zeolites. From an initial study, HY was found to be the most active solid, with an 89 % conversion being observed. Hβ was found to be essentially non-selective for the production of 2,6-DTBN over 2,7-DTBN. H-ZSM-5 gave no reaction (pores were too small to allow the reaction to occur). A low conversion (31 %) was observed with HM (Si/Al 17.5), but it was found to be the most selective catalyst. A 6.4 % yield of dialkyl product was observed, with a 2,6/2,7-ratio of 14.0. It was shown that a substantial increase in selectivity towards the favoured 2,6-DTBN was observed when dealuminated HM (treated with 8 M HCl) was employed. A 31.2 % yield of dialkyl product was observed, with a 2,6/2,7-ratio of 140. This is arguably the most selective alkylation reaction to date. By optimising the reaction parameters 2,6- DTBN was observed in a 60 % yield, although a lower selectivity was observed (2,6-/2,7- ratio of 50.6).

The *tert*-butylation of naphthalene is of limited utility for 2,6-NDA production, since it may be difficult to oxidise the *tert*-butyl groups to carboxy groups. In addition, there would be loss of six carbon atoms during this process, which is wasteful[58].

1.3.16 Alkylation of naphthalene with other alkylating groups[67-69]

Generally, the research set out in the literature is concerned with the methylation, *iso*-propylation, cyclohexylation and the *tert*-butylation of naphthalene[18-66]. There are few examples for alkylations such as ethylation, propylation and butylation set out in the literature[67-69]. For example, Takeuchi and co-workers have investigated the ethylation of naphthalene. It was found that the 2,6-selectivity was similar to that observed in the cyclohexylation of naphthalene[67].

In addition, Fellmann *et al.* reported that 2,6-selectivity was observed in the ethylation of naphthalene over H-ZSM-5. A 2,6-/2,7-ratio of 2.0 was observed[68]. More recently, Kulkarni *et al.* have investigated the vapour phase ethylation of naphthalene with ethanol[69]. It was found that CeMgY was the most selective catalyst for diethylnaphthalene. It was also reported that the modification of zeolites with alkaline earth metal cations optimises the acidity (which can reduce coke formation). The alkylation of naphthalene has also been investigated with 1-propanol and 1-butanol over HY and MCM-41[70].

1.3.17 Advantages of the direct alkylation of naphthalene for producing 2,6DMN or 2,6-DAN

Direct alkylation of naphthalene to give 2,6-dialkylnaphthalenes (2,6-DAN), holds a big advantage over the other methods proposed. The number of steps required to get to the desired 2,6-DAN product is reduced. Only two steps are required in theory to produce the product dialkylated at the 2,6-positions.

This would be advantageous in terms of the economics and the time scale of the process, although, in practice the problems presented with the possible formation of the 9 other isomers of dimethylnaphthalene overshadow this. The formation of these isomers result in difficulties in terms of their separation from the desired 2,6-isomer. Complications with isolation and purification are also observed, making the process non-economical.

A summary of past and current routes for synthesising 2,6-DMN is given in Table 1.3.1.

Table 1.3.1: Summary of past and current routes for synthesising 2,6-DMN

Company/Reagents	Catalysts Employed	No Of Steps	Final Step: Conversions and Yield of 2,6-DMN	Adv	DisAdv
Mitsubishi Gas Chem (*m*-Xylene, propene and carbon monoxide)	$AlCl_3$, raney nickel and iron oxide	**3**	**89 %** conversion in final step, **62 %** selectivity towards 2,6-DMN	Cheap, readily available reagents.	**1.**Limitations associated with Friedel-Crafts catalyst. **2.** Low yield and selectivity towards desired 2,6-DMN product
BP Amoco (*o*-Xylene and Butadiene)	Na/K2CO3 (Superbase), Zeolite Y and a noble metal catalyst on alumina, silica or activated carbon	**4**	**42 %** yield of 2,6-DMN and **40 %** yield of 1,6-DMN in final step	Cheap, readily available reagents.	**1.** Involves 4 steps, each having relatively low selectivities and conversions. **2.** Separation of 1,6- and 2,6-DMN is costly and problematic
Optatech (*p*-Xylene and Butadiene)	Zeolite NaX, Cr_2 supported on Al_2 impregnated with K_2CO_3	**2**	Conversions between **55 %** and **64 %** Selectivities towards 2,6-DMN between **24 %** and **34 %**	Fewer steps required to obtain final product	Low conversions and selectivities towards desired 2,6-DMN product
NKK, Chiyoda and Catalytica *(Naphthalene, methylating agent)*	Zeolite Mordenite	**2**	**42 %** Conversion. **72 %** Selectivity towards *2-methylnaphthalene*. **34 %** Selectivity towards *2,6-DMN*.	Fewer steps required to obtain final product	Formation of other dimethylnaphthalene isomers leading to separation and purification difficulties

1.3.18 Conclusion

It is clear there is still a great need for a superior method for the synthesis of 2,6-DMN. In an ideal world it would be possible to obtain 2,6-DMN selectively in large yields, from inexpensive readily available starting materials in one step with a catalyst that presents no problems to sanitation.

The work contained within this thesis was fuelled by the need for a superior method for producing 2,6-DMN. It was hoped to improve the selectivity towards the 2,6-isomer considerably without the formation of any other isomers of dimethylnaphthalene, and significantly improve the final yield of the desired product.

Two possible approaches have been investigated in this body of work. The first comprises the selective build up of an appropriate monocyclic compound to give the desired 2,6-DMN. The second involves the selective alkoxyalkylation of the naphthalene ring. These approaches will be discussed in turn in the following Chapters.

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Chapter 2, Part 1

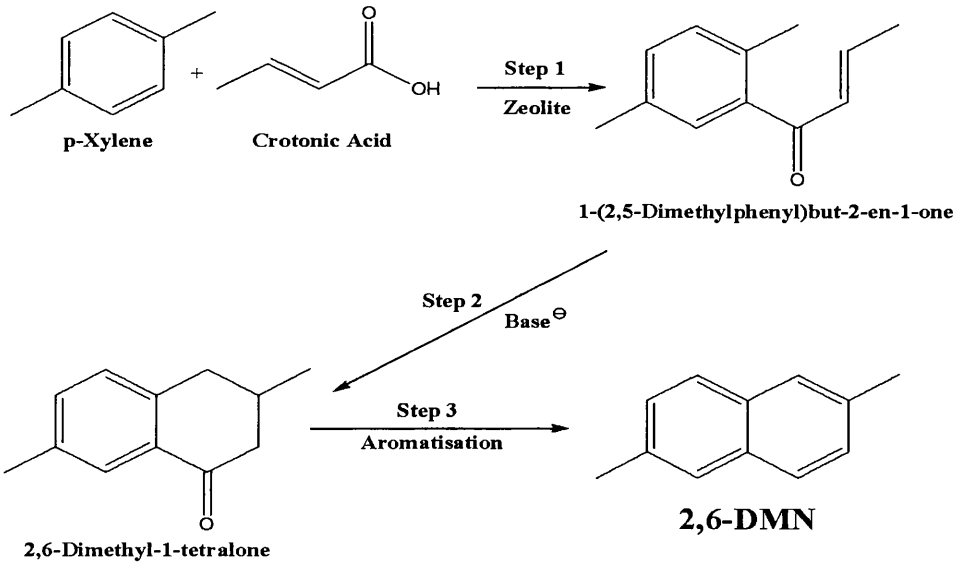
Introducing a new route for the synthesis of 2,6-DMN

2.1.1 Introduction

As discussed in Chapter 1, current methods for synthesising 2,6-DMN for use in the commercial production of PEN are severely limited, in terms of the selectivity and yield of the final product. In view of this, it was decided to investigate an alternative method for synthesising 2,6-DMN in an attempt to overcome these limitations, and improve the yield of and selectivity for the desired product.

2.1.2 Alternative method to synthesise 2,6-DMN

It was proposed to try and synthesise 2,6-DMN from *p*-xylene and crotonic acid in three acid/base catalysed steps **(Reaction scheme 2.1.1).** The first step of the process involved the zeolite catalysed acylation of *p*-xylene with crotonic acid. The second step involved the base catalysed cyclisation of the direct acylated product to give a tetralone intermediate. The third step involves overall dehydration to yield the desired **2,6-DMN** product, though it might require reduction of the carbonyl group, dehydration and then dehydrogenation.



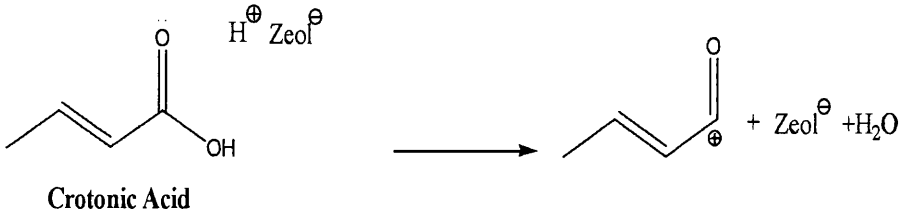
Reaction scheme 2.1.1: Proposed three stage method to synthesise 2,6-DMN

p-Xylene and crotonic acid were chosen as reagents for several reasons; they are cheap, readily available and easy to handle. In addition, the direct acylated product from the reaction of *p*-xylene and crotonic acid would yield a tetralone intermediate with methyl groups in positions 2 and 6. Therefore, an isomerisation step would be avoided when generating 2,6-DMN. Consequently, the number of steps required to produce 2,6-DMN would be reduced, increasing the industrial viability (more cost efficient) of the process in comparison to the current methods for producing 2,6-DMN (isomerisation step required in the route proposed by BP Amoco). Each step of the proposed new process will be discussed in turn in the following sections.

2.1.3 Step 1: Zeolite catalysed acylation of *p*-xylene with crotonic acid

The first step of the proposed process involved the zeolite catalysed acylation of *p*-xylene with crotonic acid in an attempt to generate **1-(2,5-dimethylphenyl)but-2-en-1-one,** via an electrophilic aromatic substitution pathway.

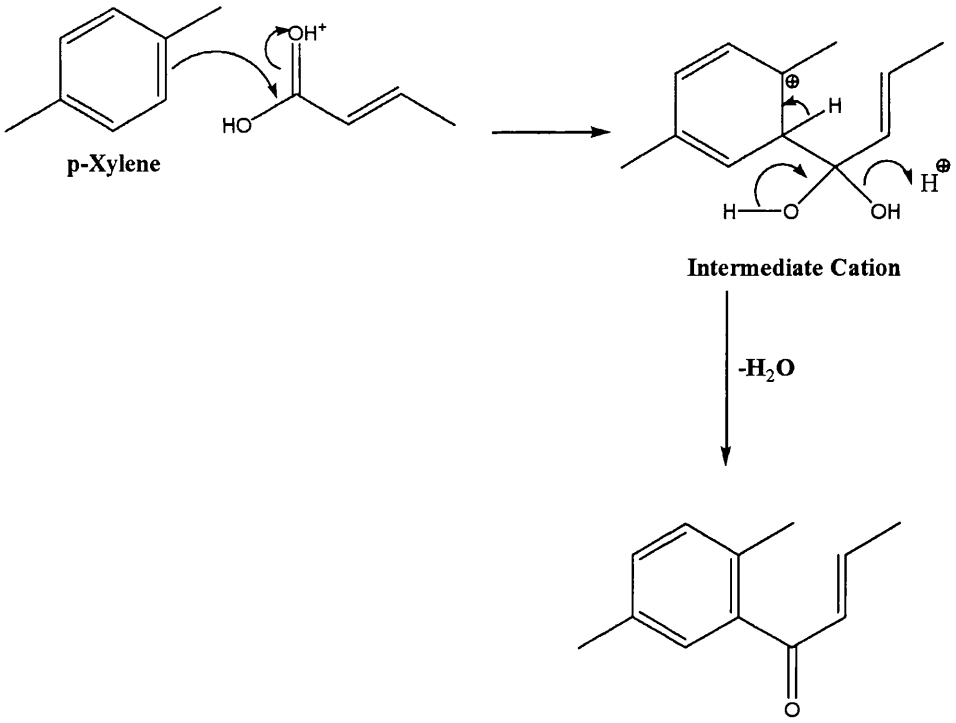
Reaction Scheme 2.1.2 illustrates how crotonic acid is protonated on treatment with an acidic zeolite catalyst to generate an electrophile.



Crotonic Acid

Reaction Scheme 2.1.2: Protonation of crotonic acid on treatment with an acidic catalyst.

The electrophile then attacks the pi electrons of the aromatic ring in *p*-xylene to generate a carbocation intermediate. Loss of hydrogen regenerates the aromatic ring to give the acylated product (illustrated in **Reaction Scheme 2.1.3**).



Reaction Scheme 2.1.3: Reaction mechanism for the acylation of *p*-xylene with crotonic acid.

2.4 The Friedel-Crafts acylation of aromatic compounds: *the traditional method for producing aromatic ketones*

Aromatic ketones are important intermediates in the manufacture of fine chemicals, pharmaceuticals and fragrances[1,2,16] and are traditionally synthesised by a Friedel-Crafts acylation reaction. (named after the chemists Charles Friedel and James Crafts who also discovered the Friedel-Crafts alkylation reactions discussed in Section **1.3.8** in Part 3 of Chapter 1).

The Friedel-Crafts reaction involves the acylation of an aromatic compound with a carboxylic acid derivative (typically an acid chloride), with a Lewis acid catalyst ($AlCl_3$, $ZnCl_2$ $FeCl_3$) or a protonic acid (HF, H_2SO_4 or HCl)[3] *via* an electrophilic substitution pathway.

In order to understand the initial step of this process (reaction of *p*-xylene and crotonic acid) and the Friedel-Crafts acylation reaction in more detail, the next section introduces aromatic compounds and the main principles of aromatic electrophilic substitution reactions.

2.1.5 Aromatic Compounds:

Aromatic compounds can be defined as planar, conjugated, cyclic molecules with sp^2-hybridised carbons. Benzene (C6H6, the parent of aromatic compounds, shown in **Figure 2.1.1**), is a cyclic compound with six sp^2-hybridised carbons (each carbon atom contributes a p orbital with one electron to a pi system), and each carbon is attached by a sigma bond to a hydrogen atom.

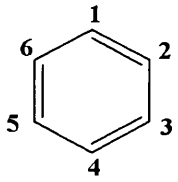


Figure 2.1.1: Structure and numbering of benzene

The carbon-carbon bond lengths in benzene are equivalent and intermediate in length between single and double bonds (parallel p-orbitals overlap continuosly making all the carbon-carbon bonds identical). The carbon-carbon bonds are 139 pm, compared to 153 pm in alkanes, and 134 pm in alkenes.

Two representations can be drawn to show the possible arrangements for the pi bonds in benzene, and are shown in **Figure 2.1.2**. They are called Kekulé structures after the German chemist Kekulé who first imagined the structure of benzene in 1865.

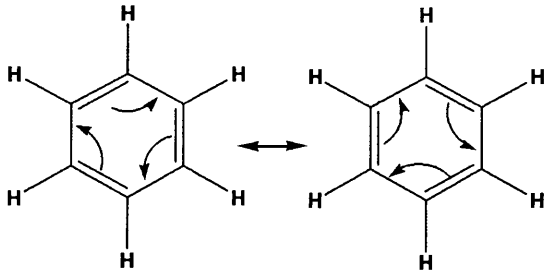


Figure 2.1.2: Resonance contributors (Kekulé structures) for benzene.

In the two representations a double bond can be placed either between C1 and C2 or between C1 and C6. As there is no energetic preference for one or the other of these representations, benzene is better represented as a combination of both of these structures

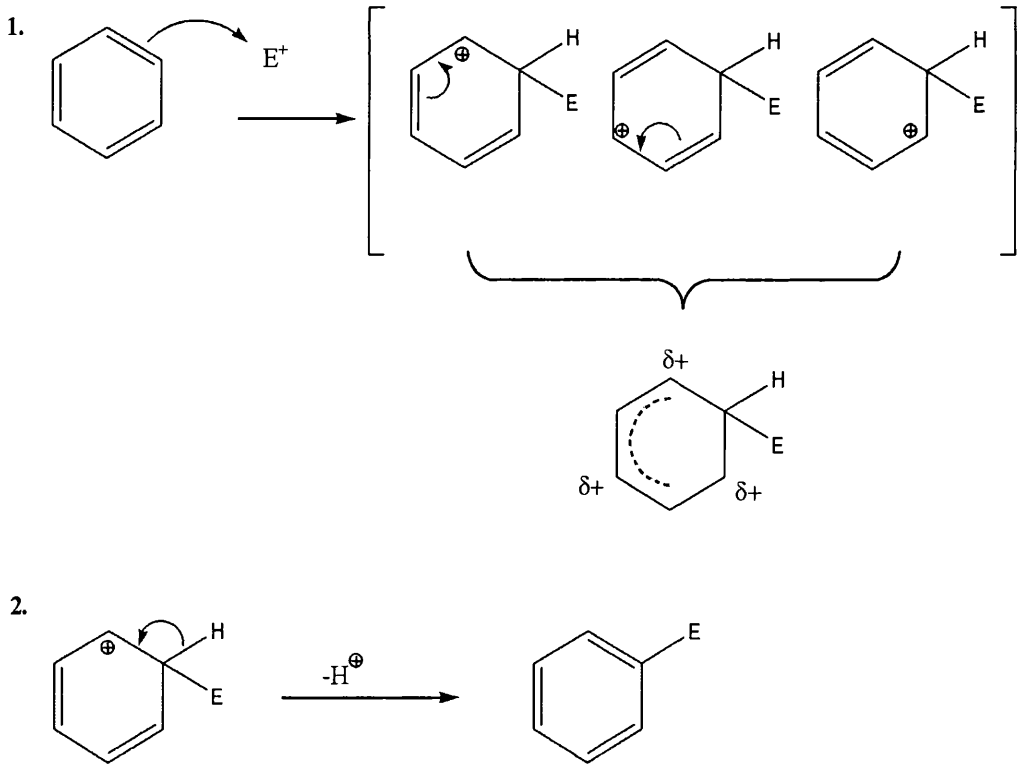
2.1.6 Electrophilic reactions of aromatic compounds

Benzene and substituted benzenes have exceptional stability. This is associated with the cyclic structure and the presence of six pi-electrons in conjugation. There is a tendency for the cyclic pi-electron arrangement to be preserved in reactions, therefore benzene does not undergo many of the electrophilic addition reactions typical of alkenes (which would destroy the aromatic ring). Instead, aromatic compounds undergo electrophilic substitution reactions by an overall substitution process (where the special electronic character of the system is preserved).

Electrophilic aromatic substitution reactions are very useful. Examples include halogenation, sulfonation, alkylation, nitration and acylation. Such reactions have applications in the pharmaceuticals industry and the synthesis of precursors for further reactions

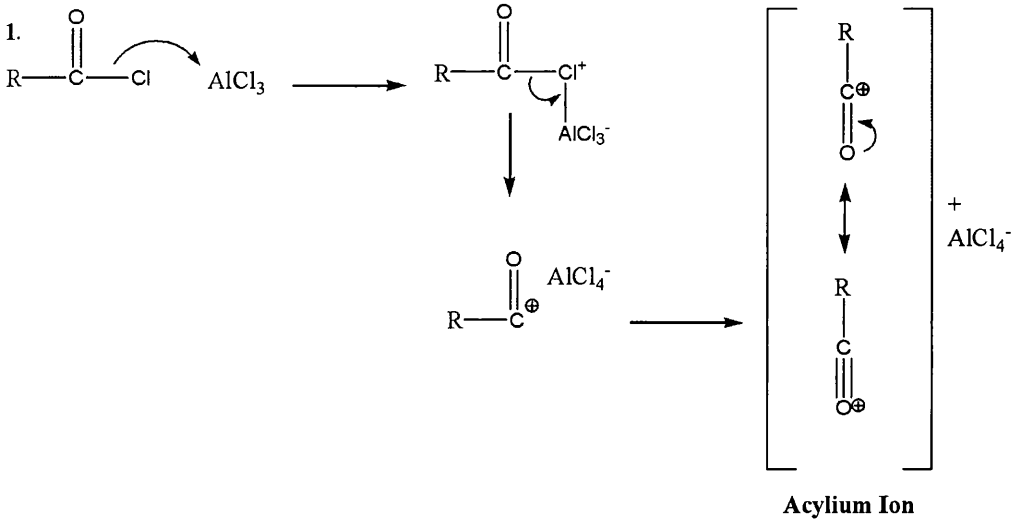
2.1.6.1 General reaction mechanism

Electrophilic substitution goes by way of a mechanism that permits the product to retain aromaticity. Firstly a positive electrophile is generated, usually on treatment with a catalyst. This is then followed by a two step substitution. In the first step the electrophile is attacked by the pi-electrons of the nucleophilic benzene ring (rate limiting step) to yield a non-aromatic carbocation intermediate in which the electrons are delocalised (stabilised by resonance). The intermediate carbocation can be represented by three significant resonance structures as shown in **Reaction Scheme 2.1.4**. In the second step, the carbocation loses a proton to yield the substitution product (benzene ring is regenerated along with aromaticity).

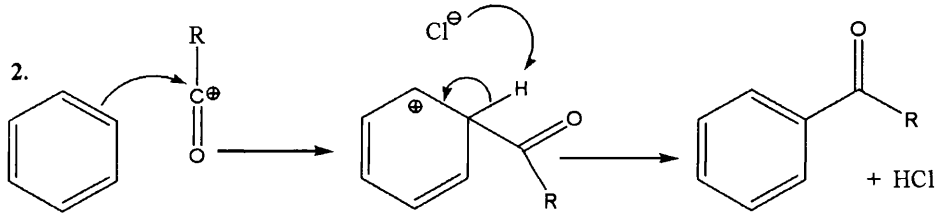


Reaction Scheme 2.1.4: General mechanism of aromatic electrophilic substitution

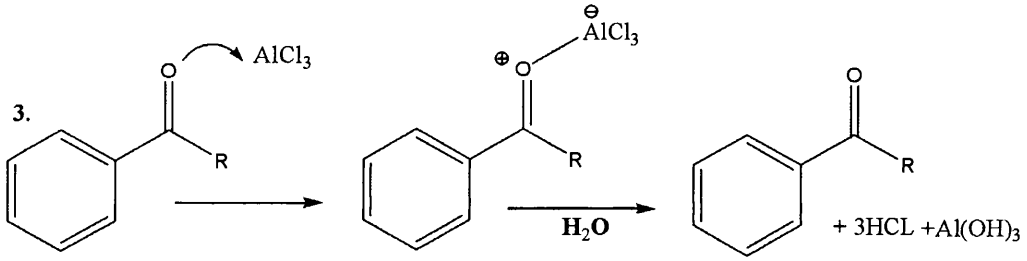
2.1.6.2 Reaction Mechanism of Friedel-Crafts Acylation Reaction:



Acylium Ion



Aromatic Ketone Product



Product Complexes With The Catalyst

Reaction Scheme 2.1.5: Reaction Mechanism for Friedel-Crafts Acylation

In the first step, the Lewis acid complexes with the chlorine atom of the acid chloride. Cleavage of the carbon-chlorine bond then generates the acylium ion. (the acylium ion bears a formal positive charge on the carbon and is stabilised by a resonance contributor that uses one of the lone pairs of oxygen to back bond forming a triple bond between carbon and oxygen (Step 1 in **Reaction Scheme 2.1.5**).

In the second step of the reaction the acylium ion attacks the aromatic ring to generate a carbocation intermediate, also stabilised by resonance (see **Reaction Scheme 2.1.4**). Loss of HCl yields the aromatic ketone product which reacts with the Lewis acid catalyst to form a strong complex between the aluminium chloride catalyst and the carbonyl function of the ketone (this complex is catalytically inactive). The aromatic ketone is liberated on hydrolysis. The consequences of this are discussed in Section **2.1.7** of this Chapter.

2.1.6.3 Orientation of substitution (reaction of substituted benzenes)

The orientation of the substitution of incoming groups, is directed by the substituent already present on the benzene ring.

If an **electron donating group** (*e.g.* hydroxy, alkoxy, amino, halogens and alkyl groups) is attached to the benzene ring, the intermediate carbocation is stabilised and will direct the incoming electrophile to the ortho and para positions of the benzene ring (and the substituents are therefore called **ortho, para directors**). The presence of an electron donating group also increases the negative character of the ring (and therefore its attractiveness to electrophiles), and activates it towards electrophilic substitution (and the substituents are therefore called **activating groups**).

If an electron withdrawing group (*e.g.* a carboxylic acid, aldehyde, ketone, cyano, nitro or sulfonyl groups) is attached to the benzene ring, the intermediate carbocation is destabilised and the incoming electrophile is directed to the meta position (and the substituents are therefore called called **meta directors**). The presence of an electron withdrawing group also decreases the negative character of the ring and deactivates it towards electrophilic substitution (and the substituents are therefore called **deactivating groups**).

With regards to disubstituted benzene compounds, the directing effects can either reinforce each other or oppose each other, and one must consider the additive effects of the two substituents on the ring (the more powerful activating group usually has dominant influence).

2.1.7 Limitations associated with the conventional Friedel-Crafts acylation reactions

There are many limitations associated with the conventional Friedel-Crafts type acylation reactions; they are not always clean and may lead to mixtures of products and more than a stoichiometric amount of catalyst is required (the aryl ketones form a 1:1 molar adduct with the catalyst).

In addition, the work up involves hydrolysis (shown in **Step 3.** of **Reaction Scheme 2.1.5**) and neutralisation to cleave the metal halide product adduct, generally leading to the destruction of the catalyst. Also a large amount of aqueous effluent is generated, causing problems with corrosion and disposal of potentially toxic waste. This corrosive reaction system requires expensive reactors and equipment for the purification of the waste gas, (consisting of HCl and chlorinated hydrocarbons), which is hazardous to health as well as to the environment. Thus, the overall process cost is very high.

Due to the limitations associated with the conventional Friedel-Crafts type catalysts, the use of solid-acid catalysts such as zeolites in aromatic acylation reactions has become very attractive. Solid catalysts allow easy separation of products, are potentially regenerable, are only required in catalytic amounts and in the case of zeolites, their shape-selective properties may allow tailoring of the reaction to specific requirements. There is also a possibility of developing a continuous process.

2.1.8 Heterogenous catalysts in the acylation of aromatics

In view of the above, considerable effort have been put into developing heterogeneously catalysed Friedel-Crafts chemistry using solid acid catalysts, with zeolites being the most studied[4-36]. A brief review of zeolite catalysed aromatic acylation reactions, reported in the literature is given in the following sections.

The earliest results were published by Geneste *et al.*[4], who studied the acylation of toluene and *p*-xylene with straight chain carboxylic acids catalysed with lanthanide-exchanged zeolites in the liquid phase. A minimum of 94 % selectivity of the *para* isomer was observed with all the acids studied and the activity was shown to be dependent on the chain length of the acid. Similar reactions over USY and ZSM-5 zeolites have also been reported in the literature[5-6].

The first industrial application of solid acid catalysts in the synthesis of aromatic ketones is reported from Spagnol *et al.*[7], where Rhodia have commercialised the acylation of anisole with acetic anhydride using zeolite catalysts.

The acylation of benzene[29], phenol[30,31], isobutylbenzene[16,17, 7,33] and toluene[4-6,32] catalysed by zeolites has been reported in the literature. In addition, the acylation of aromatic ethers like anisole[8-23], phenetole[11], veratrole[17-19] and 2-methoxynaphthalene[7, 16-17, 24-28] over zeolite catalysts have been reported. The acylation of these compounds has drawn much attention to researchers over the last decade, due to the commercial importance of the corresponding product ketones.

Para-Acylated anisole is a useful intermediate for the production of 2-(4-methoxybenzoyl)benzoic acid, the sodium salt of which is a sweetening agent [16]. *para* Acetylated veratrole is a useful intermediate for the production of vesnainone, which is a cardiotonic[16], and 2-acetyl-6-methoxynaphthalene (prepared

by acetylation of 2-methoxynaphthalene) is a precursor for the synthesis of naproxen, a non steroidal antiinflammatory drug[16].

The acylation of anisole (methoxybenzene) over zeolite catalysts has been reported with various acylating agents, including phenylacetyl chloride[12], phenylpropionyl chloride[12], acetyl chloride[11,13], acetic anhydride[11, 13-15, 17], phenylacetic acid[12] and phenylpropionic acid[12].

Corma et al. studied the acylation of anisole by phenylacetyl and phenyl propanoyl chloride catalysed by Hβ, HY and HZSM-5 zeolites[12]. Hβ was found to be the most active catalyst, little differences in the catalytic activity were observed on varying the Si/Al ratio of the Hβ.

Akira et al.[18] have studied the acylation of veratrole with propionyl chloride in the presence of Hβ zeolite. A 70 % yield of 2,4-dimethoxypropiophenone was observed after the reaction mixture was refluxed for 3 h. Jaimol *et al.*[19] have reported selective propionylation of veratrole over various zeolite catalysts, and Hβ was found to be the most effective catalyst for the selective conversion of veratrole to 3,4-dimethoxypropiophenone. It was also found that the conversion of veratrole increased on increasing the reaction time, amount of catalyst and reaction temperature, although, a decrease in conversion was observed on increasing the veratrole/propionic anhydride molar ratio.

More recently, Choudary et al.[17] have studied the acylation of anisole and veratrole with acid anhydrides using different crystall sizes of zeolite Hβ. Anisole and veratrole gave *p*-isomers exclusively with acid anhydrides (C_2-C_8) in the presence of different crystall sizes of Hβ and in all cases the conversion of anhydride was greater than 98 %.

With regards to the acetylation of 2-methoxynaphthalene, it is of particular interest if the ketone functionality can be placed at the 6 position, to give 2-acetyl-6-methoxynaphthalene, abbreviated to 2,6-(AMN), since this compound can be used as a precursor to the anti-inflammatory drug naproxen[16].

However, during acetylation reactions, 1-acetyl-2-methoxynaphthalene (1,2-(AMN)) is a predominating product, as the acetylation of 2-methoxynaphthalene occurs at the kinetically controlled 1- position. The formation of the more linear 2,6-(AMN) can be promoted by using zeolites having uniform microporous structures. In view of this, zeolite beta has been considered as the most suitable catalyst for the shape selective production of 2,6-(AMN)[24].

Harvey and Mader[25] studied the acetylation of 2-methoxynaphthalene over zeolites USY, Hβ and ZSM-12 and showed that in all cases 6-acetyl-2-methoxynaphthalene was observed as the major product.

Davis et al.[7] have investigated the acetylation of 2-methoxynaphthalene with acetic anhydride over zeolite beta, and found that zeolite beta was active for the acetylation of 2-methoxynaphthalene but with poor selectivity towards 2,6-(AMN). However, the selectivity was improved over zeolite beta samples with a larger crystal size.

Guisnet et al.[26] have found that high yields of 2,6-(AMN) can be obtained over a commercial Hβ zeolite by operating at relatively high temperature (170 °C), and in the presence of a solvent of intermediate polarity such as nitrobenzene. The selectivity towards the favoured 2,6-(AMN) at elevated temperatures can be explained in terms of the ease of attack of the acylium ion at position six, which requires a greater activation energy than attack at the very activated position one.

Lenarda et al.[27] have reported on the acylation of 2-methoxynaphthalene with acetic and propionic anhydrides catalysed by Hβ zeolite. A mixture of 1- and 6-substituted isomers was observed with both acetic and propionic anhydride. The 6/1 ratio ranged from 2.5 to 9.0, depending on the pre-treatment temperature of the zeolite and the catalyst/substrate ratio. It was reported that the selectivity towards the 6-isomer increased on increasing the pre-treatment temperature of the zeolite (due to extra framework aluminium deposition on the channel walls reducing the mobility of the more bulky molecules), the selectivity also increased when the amount of catalyst was increased.

Cheng *et al.*[28] compared Hβ, HY and HM (Hβ and HY have three dimensional channel structures and HM has a one dimensional channel structure) in the acylation of 2-methoxynaphthalene. It was shown that Hβ was more selective towards 2,6-(AMN) than HY or HM. However, the yield of 2,6-(AMN) was similar with all three catalysts at elevated temperatures (probably due to faster isomerisation of the 1-acyl isomer to the 6-acyl isomer).

The effect of the Si/Al ratio of Hβ on the acylation of 2-methoxynaphthalene was reported by Hwang and Rhee[24], who found that the selectivity towards 2,6-(AMN) improved as the Si/Al ratio increased. More recently, Kantam et al.[17] have investigated the acetylation of 2-methoxynaphthalene with acetic anhydride over different crystall sizes of Hβ. They found that micronized Ce^{3+} beta zeolite gave good yields and selectivity toward 2,6-(AMN). This was explained in terms of the increased Lewis acidity of beta zeolite by introducing Ce^{3+}, which afforded a higher selectivity towards 2,6-(AMN) because the reversible reaction of the formed 1-acetyl-2-methoxynaphthalene to 6-acetyl-2-methoxynaphthalene was promoted. As illustrated

by these examples reported in the literature, the acylation of 2-methoxynaphthae is a fine example of the shape selective catalysis provided by zeolites.

2.1.8.1 α,β-Unsaturated acids in the acylation of aromatics catalysed by solid acids

The use of α,β-unsaturated acids in the acylation of aromatics catalysed by solid acids has also been reported in the literature[32, 37, 38]. This reaction is attractive, since the possibilities of further reactions of the resultant phenylketone are increased, due to the introduction of the double bond in the side chain.

Corma et al.[32] studied the reaction of crotonic acid with *m*-xylene, *p*-xylene and toluene over heteropolyacids and large pore zeolites. Due to the conjugated system of an α,β-unsaturated acid, two cationic species coexist in the reaction media. Both species can react further with *p*-xylene to form the acylated product (**A**) or the alkylated product (**B**) (illustrated in **Figure 2.1.3**). Therefore, the preferred reaction pathway of the α,β-unsaturated acid was investigated. Furthermore, both the alkylated and acylated product are able to react further with a either a molecule of *p*-xylene or intramolecularly to form the corresponding indanone (illustrated in **Figure 2.1.4**)[32].

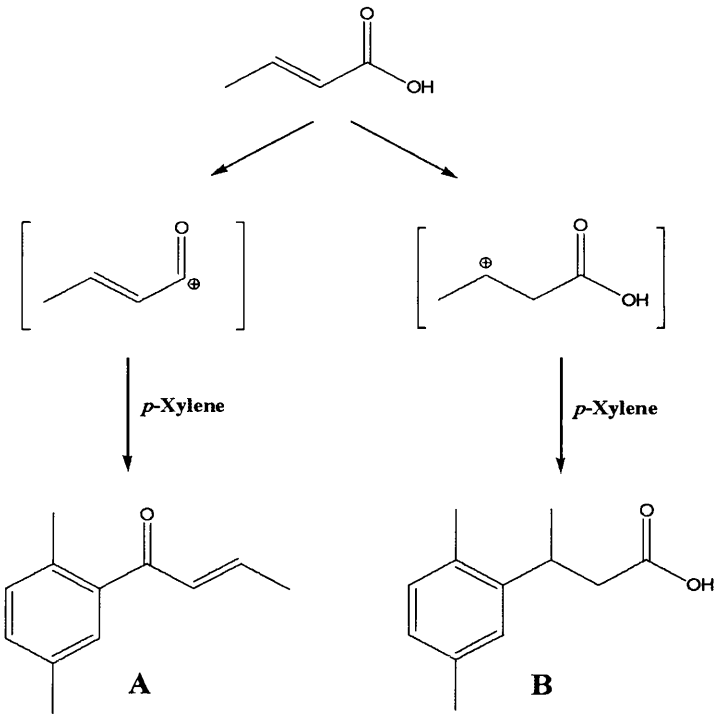


Figure 2.1.3: Possible reaction pathways for crotonic acid in the presence of an acid catalyst[32].

The influence of the catalyst acidity and the importance of active site accessibility on the catalytic activity were also investigated.

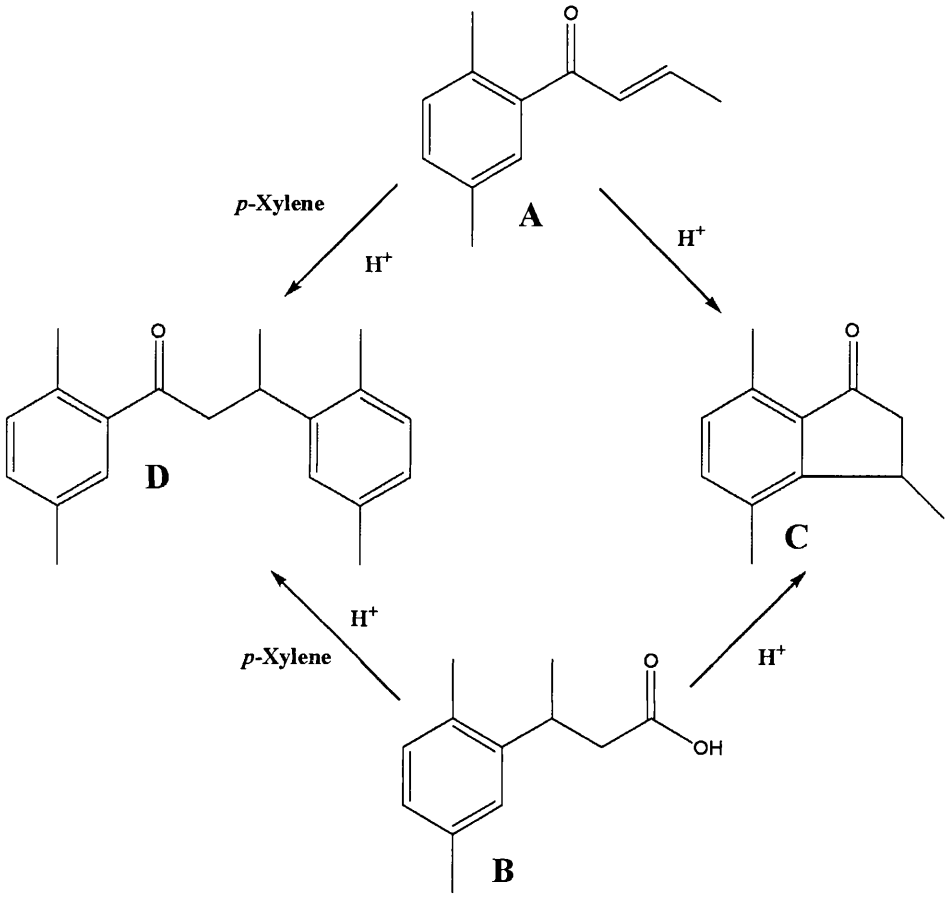


Figure 2.1.4: Further reaction possibities of acylated and alkylated *p*-xylene[32].

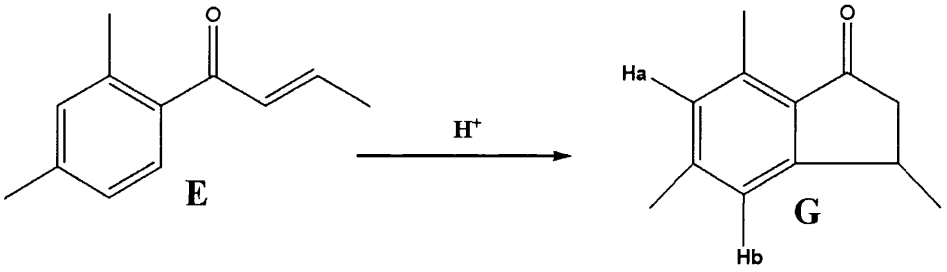
In the acylation of *p*-xylene with crotonic acid, the reactions were carried out in a batch reactor. Crotonic acid (1.16 mmol) was stirred in an excess of *p*-xylene (100 mmol) and catalyst (0.086 mmol) at the reflux temperaure of *p*-xylene. The catalyst was filtered at the end of the reaction and washed with DCM. The filtrate was analysed by NMR and GCMS in an attempt to characterise the products.

It was reported, that in the presence of the heteropolyacids small amounts of the alkylated product (**B**) (7 % yield with Cs_2HPW), small amounts of the doubly arylated product (**D**) (2 % yield with $Cs_2.5HPW$) and large yields of the indanone product (**C**) (65 % yield with HPW6) were observed. *($H_3PW_{12}O_{40}$ = phosphotungstic acid, HPW6 = heteropolyacid supported at 60 % w/w on a SiO_2 support, Cs_xHPW = cesium salt of phosphotungstic acid where $_x$ indicates the number of cesium atoms in*

the molecule). However, the acylated product (**A**) was not observed. In the presence of zeolite catalysts the conversion was much lower, a 2 % yield of the indanone being observed in the reaction with Hβ zeolite, and a 1 % yield of the biphenyl compound being observed with HY zeolite.

It was reported that when either the acylated or alkylated products of *p*-xylene were formed, they reacted quickly by a consecutive intramolecular alkylation or acylation. Consequently, the indanone was the major product observed.

It was not known how much of the indanone product came from the acylated or alkylated *p*-xylene. This was elucidated by carrying out a reaction with *m*-xylene and crotonic acid, where the indanones formed by either intramolecular alkylation of the acylated *m*-xylene (**G**) or the intramolecular acylation of the alkylated *m*-xylene (**H**) could be easily differentiated by NMR analysis, since the aromatic proton (**Hb** shown in **Figure 2.1.5**) would give a singlet signal at lower field if ortho to a carbonyl group.



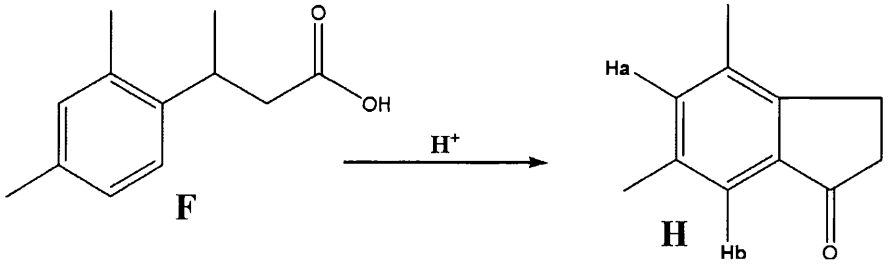


Figure 2.1.5: Structure of indanones formed by intramolecular alkylation of the acylated *m*-xylene (**G**) and the intramolecular acylation of the acylated *m*-xylene (**H**)[32].

It was found that the indanone generated in the reaction was formed by the intramolecular alkylation of the acylated *m*-xylene (3,5,7trimethyl-indanone). Therefore, this proved that the major reaction pathway under the experimental conditions used by Corma *et al.* was the acylation of the xylene followed by intramolecular alkylation by the double bond to form the corresponding indanone (the acylated product also reacted with a further molecule of xylene to give the double arylated product (**D**).

The acylation of toluene (a less activated aromatic molecule than the xylenes) was also investigated. A similar type of product distribution was observed as with the xylenes but it was found that the rate of the initial acylation and the intramolecular alkylation were slower than the xylenes.

It was concluded that the first step of the reaction pathway for the acylation of an aromatic compound with an α,β-unsaturated acid was an initial acylation, followed by intramolecular alkylation of the aromatic ring. It was also found that the rate of these reactions was strongly related to the activation of the aromatic ring rather than the formation of the protonated species (of crotonic acid). It was also observed that the heteropoly acids (CsxHPWs and HPW6s) employed in the reactions were more active than the zeolites. Furthermore, Hβ was more active than HY in the acylation of xylene with crotonic acid.

The research group in Valencia led by Corma has also investigated the acylation of anisole[37] (which has a highly activated aromatic ring). It was found that intermolecular reactions were favoured when activated aromatic compounds such as

anisole were employed. It was reported that the product resulting from an initial acylation suffered a further alkylation reaction.

Even though in the work of Corma's group low conversions of crotonic acid were observed and the desired acylated product was not observed, in zeolite catalysed reactions of *p*-xylene with crotonic acid, it was felt that the reaction was worthy of further and more thorough investigation because of the potential use of the direct acylated product in the synthesis of 2,6-DMN. It was hoped to optimise the reaction in an attempt to maximise the yield of the direct acylated product (to be used in the second step in producing 2,6-DMN), whilst inhibiting the formation of the undesirable indanone product. Heteropoly acids were not investigated since they were found to be more active than zeolites Hβ and HY and gave high yields of the undesirable indanone product. The following Sections therefore report the results of our own investigation of this reaction.

2.1.9 Initial Results of the zeolite catalysed acylation of *p*-xylene with crotonic acid

Two reactions were carried out whereby *p*-xylene (500 mmol) was reacted with crotonic acid (5.8 mmol) in the presence of either Hβ or HY zeolites (2.0 g). The reaction mixture was refluxed for 3 h at 138 °C (reflux temperature of *p*-xylene). After the given reaction time the catalyst was filtered at the pump and washed with dichloromethane. The filtrate and washings were combined and analysed by GC, which illustrated that the desired reaction had not taken place, with *p*-xylene and crotonic acid being recovered quantitatively.

2.1.10 Attempts to increase the conversion of crotonic acid

In an attempt to promote the desired reaction and increase the conversion of crotonic acid to generate the direct acylated product, reactions were carried out under more forcing conditions. Experiments were conducted with Hβ and HY in which the reaction time was increased to 6 h and 12 h, using the same procedure as described in Section **2.1.9**. An increase in the conversion of crotonic acid was not observed, and *p*-xylene and crotonic acid were recovered quantatively.

Further experiments were carried out in which the amount of catalyst was increased to 4.0 g and 6.0 g (using the same procedure as described in Section **2.1.9**), but GC analysis of the reaction mixture showed once again that the reaction had not occurred.

2.1.10 Discussion

If you take the results reported by Corma *et al.* into account[32], it was disappointing but not surprising that the desired reaction did not take place. However, one would have expected small amounts of the acylated or indanone product to be observed, especially under more forcing conditions (based on the results reported in the literature where a 2 % yield of indanone was observed with Hβ).

This can be explained by two factors; firstly the reaction conditions described in the literature were not replicated in exact terms in the labs in Swansea. Corma *et al.* referred to a "batch reactor" in which they carried out their reactions, but how this compares with our reactions which were carried out using simple reflux apparatus is not known. Secondly, the zeolites employed in our reactions may have been different to the zeolites used by *Corma et al.* in terms of their Si/Al ratio, as the Si/Al ratio of the zeolites were not reported in the literature. This would mean that the activity of

the zeolites reported in the literature would be different to the activity of the zeolites employed in our reactions.

One can conclude that Hβ (Si/Al 12.5) and HY (Si/Al 30) were not sufficiently active to facilitate the reaction between *p*-xylene and crotonic acid, under the conditions employed. In view of this, it was decided not to carry out an in depth optimisation study of the zeolite catalysed acylation of *p*-xylene with crotonic acid any further at this stage. Furthermore, it was decided to synthesise the aromatic ketone intermediate using the traditional Friedel-Crafts method, to allow the second stage of the reaction to be monitored. This reaction is discussed in more detail in Part 2 of this Chapter.

2.1.12 Experimental

2.1.12.1 General experimental

All instrumentation, analytical methods and reagents employed are included as an appendix.

2.1.12.2 Typical experimental procedure

Reaction of p-xylene and crotonic acid with zeolite catalysts

Heating and stirring of reaction mixture were achieved by means of a magnetic stirrer hot-plate, an oil bath and an internal magnetic follower. The temperature of the oil bath was controlled by a contact thermometer. A magnetic stirrer bar was placed inside a round bottomed flask (500 ml) which was then charged with *p*-xylene (53.76 g, 507 mmol), crotonic acid (0.501 g, 5.8 mmol) and freshly calcined zeolite (2.0 g). The stirred mixture was refluxed at 138 °C (reflux temperature of *p*-xylene) for 3 h. After the given reaction time the reaction mixture was cooled to room temperature and the catalyst was filtered using a sinter funnel at the pump. The spent catalyst was washed with DCM (3 x 20 ml) to ensure maximum extraction of organic material from the solid. The filtrate and washings were combined and subjected to GC analysis.

2.1.12.3 Calcination of zeolite catalyst

Hβ (Si/Al 12.5) and HY (Si/Al 15.0) were calcined at 500 °C for 24 h, prior to use in the reactions.

2.1.13 GC analysis

Product mixtures were analysed by gas chromatography. A 1 μl sample was injected using a splitless technique.

The injector and detector temperature were set at 300 °C. Tetradecane was used as the internal standard. Helium was used as the carrier gas at a pressure of 9 psi. The GC conditions used for the analysis are shown in **Figure 2.1.6**.

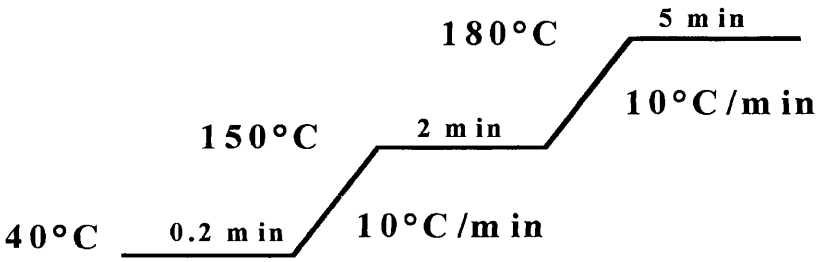


Figure 2.1.6: The GC conditions used for analysis of the product mixtures from the zeolite catalysed reactions of *p*-xylene and crotonic acid.

The GC traces of the product mixtures under these conditions gave two peaks with retention times of 2.51 min and 4.79 min, corresponding to *p*-xylene, and crotonic acid, respectively.

2.1.14 Quantification of products - calculating response factors

Response factors for *p*-xylene and crotonic acid were calculated using pure samples (supplied by Aldrich). The relative amounts of *p*-xylene and crotonic acid present in each reaction mixture were then quantified. Crude products were made up in a solution of known volume along with a known amount of internal standard and injected into the GC for analysis (conditions for analysis are outlined in **Section 2.1.13**). The amounts of recovered reagents were calculated using the equations outlined in **Figure 2.1.7.**

$$\text{Rf of compound} = \frac{\text{Weight of Internal Standard}}{\text{Weight of Compound}} \times \frac{\text{Area of Compound}}{\text{Area of Standard}}$$

$$\text{Weight of compound} = \frac{\text{Weight of Internal Standard}}{\text{Rf of compound}} \times \frac{\text{Area of Compound}}{\text{Area of Standard}}$$

Figure 2.1.7: Equations used to quantify products formed.

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Chapter 2, Part 2

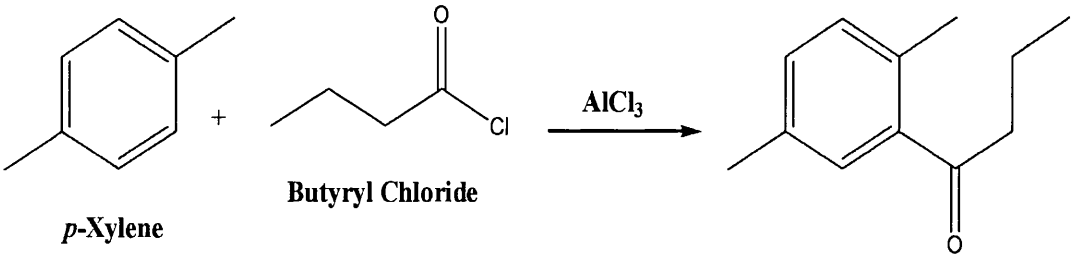
Synthesis of 1-(2,5-dimethylphenyl)but-2-en-1-one by a Friedel-Crafts acylation reaction

2.2.1 Introduction

In Part 1 of this Chapter, it was shown that the zeolite catalysed reaction of *p*-xylene and crotonic acid failed to give the aromatic ketone product. In view of this, it was decided to synthesise the aromatic ketone using the traditional Friedel-Crafts acylation method using a Lewis acid catalyst. Even though Friedel-Crafts reactions are limited (limitations discussed in Section **2.1.7** in Part 1 of this Chapter), it was hoped the acylated product would be obtained in a reasonable yield to allow the second stage of the reaction (base catalysed cyclisation of the aromatic ketone to give a tetralone intermediate) to be monitored.

2.2.2 Reaction of butyryl chloride and *p*-xylene catalysed by aluminium chloride

It was decided to carry out an initial reaction with butyryl chloride and *p*-xylene catalysed by aluminium chloride (**Reaction Scheme 2.2.1**), as these reagents were already available in the lab. The reaction mechanism for Friedel-Crafts acylation of aromatic compounds is discussed in Section **2.1.6.2** in Part 1 of this Chapter.



p-Xylene + **Butyryl Chloride** → **1-(2,5-dimethylphenyl)butan-1-one**

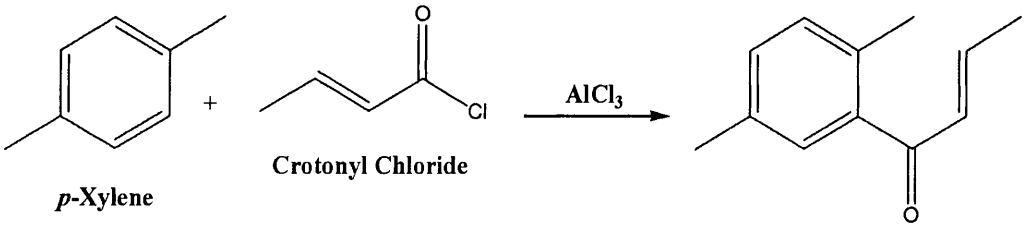
Reaction Scheme 2.2.1:

The reaction was carried out based on a procedure set out in the literature[1]. Butyryl chloride (1.08 g, 10 mmol) was stirred in an excess of *p*-xylene (36.7 g, 346 mmol) with two equivalents of aluminium chloride (1.25 g, 20 mmol), at room temperature for 3 h under an inert atmosphere. The reaction was quenched by addition

of 2 M $NaHCO_3$ solution, the solid formed was filtered at the pump and the filtrate was separated into aqueous and organic fractions. The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and dried over magnesium sulfate. Solvents were evaporated at the pump and *p*-xylene was removed by reduced pressure distillation, to afford the acylated product in a 54 % yield. Purity was checked by GC and the structure of 1-(2,5-dimethylphenyl)butan-1-one was confirmed by NMR and MS analysis.

2.2.3 Reaction of crotonyl chloride and *p*-xylene catalysed by aluminium chloride

In an attempt to introduce unsaturation into the aromatic ketone product, and increase the ability of the ketone to cyclise on treatment with base (to give the tetralone intermediate), a reaction of crotonyl chloride and *p*-xylene catalysed by aluminium chloride (**Reaction Scheme 2.2.2.**) was carried out.



p-Xylene

Crotonyl Chloride

1-(2,5-dimethylphenyl)but-2-en-1-one

Reaction Scheme 2.2.2:

Crotonyl chloride (1.06 g, 10 mmol) was stirred in an excess of *p*-xylene (36.76 g, 347 mmol) with two equivalents of aluminium chloride (1.27 g, 20 mmol), under the same reaction conditions and using the same procedure as described in Section **2.2.2**. A residual oil (0.98 g) was obtained which comprised of two spots on TLC analysis. Separation of the products by column chromatography allowed pure materials to be obtained.

The first spot on TLC analysis corresponded to the direct acylated product, 1-(2,5-dimethylphenyl)but-2-en-1-one. The second spot corresponded to the indanone product, 3,4,7-trimethyl-1-indanone. Confirmation of the structures of 1-(2,5-dimethylphenyl)but-2-en-1-one and 3,4,7-trimethyl-1-indanone (**Figure 2.2.1**) was provided by NMR and MS analysis. The yield of acylated product was around 41 % and the yield of indanone was around 4 %.

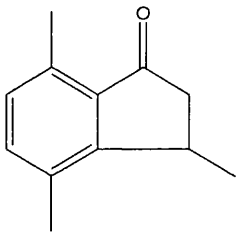


Figure 2.2.1: 3,4,7-Trimethyl-1-indanone

2.2.4 Yield optimisation of 1-(2,5-dimethylphenyl)but-2-en-1-one formation

It was decided to carry out a series of reactions in an attempt to optimise the yield of the desired acylated product, and inhibit the yield of the undesirable indanone product. This should allow the acylated product to be isolated in reasonable yield for further reaction.

2.2.4.1 Investigating different reaction parameters

It was proposed to carry out a series of optimisation reactions in which several reaction parameters would be varied. These included reaction temperature, the amount of catalyst employed, the type and volume of solvent employed, and the length of reaction. The results are discussed in the following sections.

GC analysis of the first product mixture did not indicate unreacted crotonyl chloride. It was thought that crotonyl chloride was removed from the system in the work up of the reaction (i.e. on addition of $NaHCO_3$ solution or during the process of

removal of solvents or *p*-xylene). Therefore, unreacted crotonyl chloride was not measured.

2.2.4.2 Effect of reaction temperature on product yield

In the reaction described in Section **2.2.3**, it was noted that on mixing the reagents an increase in temperature was observed that was sufficiently high enough for the reaction mixture to reflux. It was thought that this increase in temperature may have encouraged the formation of the indanone compound via an intramolecular alkylation of the acylated compound[2].

In an attempt to determine the effect of reaction temperature on the products formed, a series of reactions was carried out in which the reaction temperature was varied from 0 °C to 30 °C using the same procedure described in Section **2.2.2.** The results are reported in Table 2.2.1. The amount of residual oil observed after the reaction work up is reported in grams (g). The relative amounts of acylated and indanone products contained in the residual oil are also reported as % yields. The equations used for determining the % yields of the respective products are given in Section **2.2.8**.

When the reaction was carried out at 0 °C, by submersion of the round bottom flask in an ice bath, 43 % of the acylated product was observed and the product was free of indanone. A reaction was then carried out in which the reaction mixture was cooled in an ice bath for the initial mixing of the reagents, and the first hour of the reaction. The temperature was then gradually increased to room temperature, and the reaction mixture was stirred for a further two hours. The acylated product was observed in a 50 % yield, still free from the formation of indanone. This reaction suggests that cooling the reaction in the early stages inhibits the formation of the

undesirable indanone, which was observed in a 6 % yield when the reaction was carried out at room temperature for 3 h (in addition to 52 % of the acylated product).

Table 2.2.1: Effect of reaction temperature on the yield of the products in the reaction of *p*-xylene and crotonyl chloride over $AlCl_3$[a]

Reaction Temperature (°C)	0 °C	0 °C 60min, RT 120min	RT	30 °C
Amount of product recovered (g)[b]	0.75	0.87	1.02	1.64
Acylated (%)[c]	43	50	52	74
Indanone (%)[c]	0	0	6	20
Total (%)[c]	43	50	58	94

[a] 3 h stirred reactions at various temperatures; $AlCl_3$ (1.27 g, 20 mmol), crotonyl chloride (1.06 g, 10 mmol) and *p*-xylene (36.76 g, 347 mmol).
[b] Residual oil recovered after the removal of solvents in the work up of the reaction, expressed to 2 decimal places.
c Proportions determined by GC. Numbers expressed as percentages have been rounded to the nearest whole number.

An increase in product formation was observed when the reaction temperature was increased to 30 °C, with a 74 % yield of acylated product and a 20 % yield of indanone being observed. One can conclude that the yield of acylated and indanone products increased on increasing the reaction temperature, to a point where the reaction neared completion (94 % total product yield) when the reaction mixture was stirred at 30 °C. This demonstrates that crotonyl chloride was not chemically changed or deactivated during the course of the reaction, and it was not observed on GC analysis of the product mixture because it was removed from the system in the work up of the reaction.

It was decided that all further reactions would be carried out with the reaction mixture being cooled in an ice bath on the mixing of the reagents and for the first hour

of the reaction, then at room temperature for the remaining reaction time. The next step was to vary the amount of catalyst.

2.2.4.3 Effect of catalyst amount on product yield

It is known that more than a stoichiometric amount of aluminium chloride catalyst is required for Friedel-Crafts acylation reactions[3]. In an attempt to improve the yield of the desired product, a series of reactions was carried out to determine the effect of catalyst amount on product yield. Reactions were carried out with 5 mmol (half an equivalent), 10 mmol (1 equivalent), 20 mmol (2 equivalents) and 30 mmol (3 equivalents) of aluminium chloride. Reactions were carried out using the same procedure described in Section **2.2.4.2**, and the results are reported in Table 2.2.2.

Table 2.2.2: Effect of catalyst amount on the yield of the acylated and indanone products in the reaction of *p*-xylene and crotonyl chloride over $AlCl_3$[a]

Amount of catalyst (g)	1/2 Equivalent (5 mmol)	1 Equivalent (10 mmol)	2 Equivalents (20 mmol)	3 Equivalents (30 mmol)
Amount of product recovered (g)[b]	0.30	0.37	0.87	1.71
Acylated (%)[c]	17	21	50	85
Indanone (%)[c]	0	0	0	13
Total (%)[c]	17	21	50	98

[a] 3 h stirred reactions at 0 °C for 1 h, then room temperature for remainder of reaction; $AlCl_3$ (varying amounts), crotonyl chloride (1.06 g, 10 mmol) and *p*-xylene (36.76 g, 347 mmol).
[b,c] As Table 2.2.1.

When the reaction was carried out in the presence of 5 mmol of aluminium chloride, a 17 % yield of acylated product was observed, which increased to a 21 %

yield when 10 mmol of aluminium chloride was employed. The yield of acylated product increased even further when 20 mmol of catalyst was employed, with a 50 % yield of acylated product being observed. The indanone side product was not observed in any of these reactions. Increasing the amount of catalyst to 30 mmol brought about a significant increase in the yield of acylated product, with an 85 % yield being observed. In addition, however, the indanone was observed in a 13 % yield.

These reactions illustrated that there is a direct relationship between the amount of catalyst employed and product formation. It was also shown that the indanone was not observed when less than 30 mmol of catalyst was employed. In view of this, it was decided to carry out further reactions with 20 mmol of aluminium chloride, in order to achieve an optimum yield of acylated product without the formation of the undesirable indanone.

2.2.4.4 Effect of solvent on product yield

All previous reactions were carried out in an excess of *p*-xylene (347 mmol), which acted as the solvent as well as the reagent in the reaction. It was decided to carry out an experiment with crotonyl chloride (10 mmol) and *p*-xylene (20 mmol), stirred in an excess of DCM (40 ml), in an attempt to determine the effect of the solvent on product yield. The reaction was carried out using the same procedure as described in Section **2.2.4.2.**, and compared to the reaction where excess *p*-xylene (347 mmol) was employed. The results are reported in Table 2.2.3.

A 50 % yield of acylated product, free from indanone, was observed when the reaction was carried out in an excess of *p*-xylene, When the reaction was carried out with *p*-xylene (20 mmol) and crotonyl chloride (10 mmol) in DCM (40 ml), the yield of acylated product increased to 75 % yield (and indanone was not observed). In view of this, further reactions were carried out with DCM as solvent.

Table 2.2.3: The effect of solvent on the yield of the acylated and indanone products in the reaction of *p*-xylene and crotonyl chloride over $AlCl_3$[a]

Solvent	*p*-xylene (40 ml)	DCM (40 ml)
Amount of product recovered (g)[b]	0.87	1.31
Acylated (%)[c]	50	75
Indanone (%)[c]	0	0
Total (%)[c]	50	75

[a] 3 h stirred reactions at 0 °C for 1 h, then room temperature for remainder of reaction; $AlCl_3$ (1.27 g, 20 mmol), crotonyl chloride (1.06 g, 10 mmol), *p*-xylene (36.76 g, 347 mmol) and varying solvent (40 ml).
[b,c] As Table 2.2.1.

2.2.4.5 Effect of decreasing the volume of DCM

A reaction was carried out with crotonyl chloride (10 mmol) and *p*-xylene (20 mmol) in the presence of 25 ml of DCM, catalysed by aluminium chloride, and compared to the analogous reaction that employed 40 ml of DCM. The reaction was otherwise carried out using the same procedure as described in Section **2.2.2** and the results are reported in Table 2.2.4.

In the reaction that employed 40 ml of DCM, the acylated product was observed in a 75 % yield (indanone was not observed). When the volume of DCM was decreased to 25 ml, the yield of the acylated product increased, with an 88 % yield being observed (and indanone was still not observed). Further reactions were therefore carried out with 25 ml of DCM.

Table 2.2.4: Effect of solvent volume on the yield of the acylated and indanone products in the reaction of *p*-xylene and crotonyl chloride over $AlCl_3$[a]

Solvent	DCM (40 ml)	DCM (25 ml)
Amount of product recovered (g)[b]	1.31	1.53
Acylated (%)[c]	75	88
Indanone (%)[c]	0	0
Total (%)[c]	75	88

[a] 3 h stirred reactions at 0 °C for 1 h, then room temperature for remainder of reaction; $AlCl_3$ (1.27 g, 20 mmol), crotonyl chloride (1.06 g, 10 mmol), *p*-xylene (2.12 g, 20 mmol) and DCM (varying amounts) as solvent.
[b,c] As Table 2.2.1.

2.2.4.6 Effect of increasing the time of reaction

In an attempt to push the reaction to completion, without the formation of indanone, a series of reactions was carried out in which the reaction time was increased from 60 min (1 h) to 720 min (12 h), and compared to the reaction that was carried out for 180 min (3 h). The reactions were otherwise carried out using the same procedure as described in Section **2.2.4.2** and the results are reported in Table 2.2.5.

When the reaction was carried out for 60 min the acylated product was observed in a 19 % yield, with the indanone not being observed. When the reaction time was increased to 90 min, a significant increase in the yield of acylated product was observed (86 % yield of acylated observed, without the formation of indanone). The yield of acylated product increased only slightly when the reaction time was increased to 180 min or longer, with an 88 % yield being observed at 180 min (without the formation of indanone) and only 91 % yield of acylated product at 720

min. Unfortunately, indanone was also observed when the reaction time was increased beyond 180 min and at 720 min its yield was up to 5 %.

Table 2.2.5: Effect of increasing reaction time on the yield of the acylated and indanone products in the reaction of *p*-xylene and crotonyl chloride over $AlCl_3$[a]

Reaction Time (min)	60	90	180	360	720
Amount of product recovered (g)[b]	0.33	1.5	1.53	1.57	1.67
Acylated (%)[c]	19	86	88	89	91
Indanone (%)[c]	0	0	0	1	5
Total (%)[c]	19	86	88	90	96

[a] Stirred reactions at 0 °C for 1 h, then room temperature for remainder of reaction at various reaction times; $AlCl_3$ (1.27 g, 20 mmol), crotonyl chloride (1.06 g, 10 mmol), *p*-xylene (2.12 g, 20 mmol) and DCM (25 ml) as solvent.
[b,c] As Table 2.2.1.

In summary, these results show that the majority of the reaction occurred before 90 min. However, product formation increased on increasing the reaction time further though at a slower rate It was also shown that the indanone side product was only generated when the reaction time exceeded 180 min.

2.2.4.7 Optimum reaction conditions

In conclusion, the maximum yield of acylated product without the formation of indanone was 88 %, when crotonyl chloride (10 mmol) was stirred with *p*-xylene (20 mmol), aluminium chloride (20 mmol) and DCM (25 ml) for 180 min.

2.2.5 Summary and conclusions

An initial reaction was carried out with butyryl chloride and *p*-xylene catalysed by aluminium chloride with the direct acylated product being observed in a 54 % yield. It was decided to introduce unsaturation into the product to increase the feasibility of cyclisation to give a tetralone intermediate, in the second step in the synthesis of 2,6-DMN. A reaction with crotonyl chloride and *p*-xylene catalysed by aluminium chloride was carried out to yield the direct acylated product, but an undesirable indanone side product was also formed. An optimisation study was then conducted in an attempt to increase the yield of the acylated product and inhibit the production of the indanone.

Increasing the reaction temperature resulted in an increased yield of acylated and indanone product. Increasing the amount of catalyst resulted in an increased yield of acylated and indanone products. Employing dichloromethane as solvent resulted in an increased yield of acylated product without the formation of indanone. Decreasing the volume of dichloromethane resulted in an increased yield of acylated product, still without the formation of indanone, presumably due to a simple concentration effect. Increasing the reaction time resulted in an increased yield of acylated and indanone products.

The highest yield of 1-(2,5-dimethylphenyl)but-2-en-1-one, in the absence of any indanone was 88 %. This was achieved when crotonyl chloride (10 mmol) was stirred with *p*-xylene (20 mmol) and aluminium chloride (20 mmol) in the presence of

DCM (25 ml) for 180 min, with the reaction mixture being cooled in an ice bath for the initial mixing of the reagents and for the first hour of the reaction. The reaction mixture was then stirred at room temperature for the remaining 120 min. The yield of acylated product could be raised further by employing larger reaction times, but the indanone product was then also formed

In conclusion, under more forcing conditions the reaction proceeded towards completion. The acylated product could be obtained in reasonable yield, free from the formation of indanone, under minimum conditions. At this stage, therefore, it was decided to attempt the second step in the synthesis of 2,6-DMN, which involved the cyclisation of the acylated product in the presence of base. This is discussed in more detail in Part 3 of this Chapter.

2.2.6 Experimental

2.2.6.1 General experimental

All instrumentation, analytical methods and reagents employed are included as an appendix.

2.2.6.2 Synthesis of 1-(2,5-dimethylphenyl)butan-1-one from p-xylene and butyryl chloride

Stirring of the reaction mixture was achieved by means of a magnetic stirrer and a internal magnetic follower. A solution of butyryl chloride (1.08 g, 10 mmol) and *p*-xylene (2.12 g, 20 mmol) was added dropwise over 20 min to aluminium chloride (1.25 g, 20 mmol) covered with *p*-xylene (34.64 g, 327 mmol) in a 200 ml double necked round bottomed flask fitted with a magnetic stirrer bar and a dropping funnel. The solution was stirred for 3 h under argon, at room temperature. After the given reaction time the reaction was quenched with 2 M $NaHCO_3$ solution (100 ml) and the solid formed was filtered at the pump. The filtrate was separated into aqueous and organic layers and the aqueous layer was extracted with diethyl ether (3 x 25 ml) and the combined organic extracts were washed with water (2 x 25 ml) and then dried over magnesium sulfate. Solvents were evaporated at the pump and *p*-xylene was removed by reduced pressure distillation, to leave the acylated product (Brown oil, 0.95 g, 54 % yield).

2.2.6.3 Synthesis of 1-(2,5-dimethylphenyl)but-2-en-1-one from p-xylene and crotonyl chloride (Typical experimental procedure).

(For the reaction that was carried out at 30 °C (Table 2.2.1), heating of the reaction mixture was achieved by a hot-plate and an oil bath. The temperature of the oil bath was controlled by a contact thermometer).

A solution of crotonyl chloride (1.06 g, 10 mmol) and *p*-xylene (2.13 g, 20 mmol) was added dropwise over 20 min to aluminium chloride (1.27 g, 20 mmol) covered with *p*-xylene (34.67 g, 327 mmol) in a 200 ml double necked round bottomed flask fitted with a magnetic stirrer bar and a dropping funnel. The same reaction procedure and work up was employed as described in Section **2.2.6.2**.

After the reaction work up a residual oil (0.98 g) was obtained, which comprised two spots on TLC analysis. The crude product was subjected to column chromatography on silica eluted with hexane:diethyl ether (90:10). The two components were separated, and it was shown that the first spot corresponded to the desired acylated product and the second spot corresponded to an indanone by product.

2.2.7 GC analysis

Product mixtures were analysed by gas chromatography. A 1 μl sample was injected using a splitless technique. The injector and detector temperatures were each set at 300 °C. Tetradecane was used as the internal standard. Helium was used as the carrier gas at a pressure of 9 psi.. The GC conditions used for the analysis were the same as described in **Figure 2.1.6** in Part 1 of Chapter 2.

In the reaction of *p*-xylene and butyryl chloride catalysed by aluminium chloride, the GC trace of the product mixture under the conditions described in **Figure 2.1.6** (Part 1 of Chapter 2) gave one peak with retention time 12.9 min, which corresponded to the aromatic ketone product (1-(2,5-dimethylphenyl)butan-1-one).

In the reaction of *p*-xylene and crotonyl chloride catalysed by aluminium chloride, the GC trace of the product mixture under the conditions outlined in **Figure 2.1.6** (Part 1 of Chapter 2) gave two peaks with retention times of 13.42 min and 14.34 min, corresponding to the aromatic ketone product (1-(2,5-dimethylphenyl)but-2-en-1-one) and the indanone by product (3,4,7-trimethyl-1-indanone), respectively.

2.2.8 Quantification of products

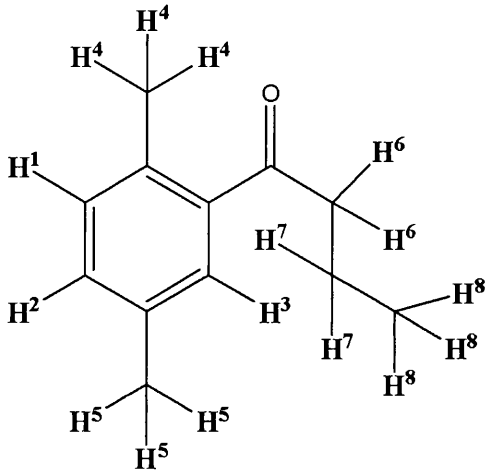
Response factors for (1-(2,5-dimethylphenyl)butan-1-one), 1-(2,5-dimethylphenyl)but-2-en-1-one and 3,4,7-trimethyl-1-indanone were calculated using pure samples isolated from the crude reaction mixtures. The relative amounts of products in each reaction mixture were then quantified using the equation set out in **Figure 2.1.7** in Part 1 of Chapter 2.

Crude products (residue obtained after work up of the reaction) were made up in a solution of known volume, along with a known amount of internal standard and injected into the GC for analysis (conditions for analysis are outlined in **Section 2.2.7**). The amount of unreacted crotonyl chloride was not quantified because it was destroyed in the work up of the reaction.

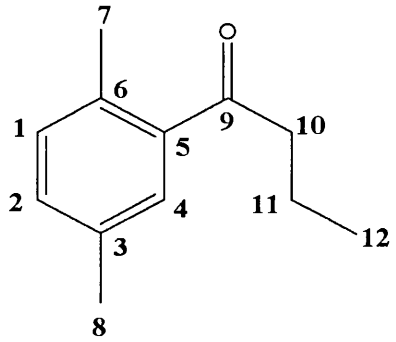
2.2.9 Analytical Data

1-(2,5-Dimethylphenyl)butan-1-one

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent.



$\delta^{1}H$: 7.42 (1H, s, H^3), 7.21 (1H, d, J = 7 Hz, H^2), 7.15 (1H, d, J = 7 Hz, H^1), 2.81 (2H, t, J = 7 Hz, H^6), 2.33 (3H, s, H^4), 2.24 (3H, s, H^5), 1.66 (2H, m, H^7), 0.93 (3H, t, J = 7 Hz, H^8).



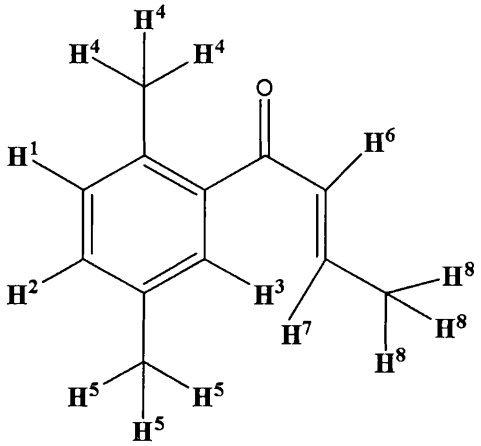
$\delta^{13}C$: 207.3 (C^9), 139.9 (C^5), 135.9 (C^6), 134.1 (C^3), 133.3 (C^4), 133.2 (C^2), 130.7 (C^1), 45.0 (C^{10}), 21.5 (C^7), 21.3 (C^8), 19.3 (C^{11}), 14.6 (C^{12}).

MS:

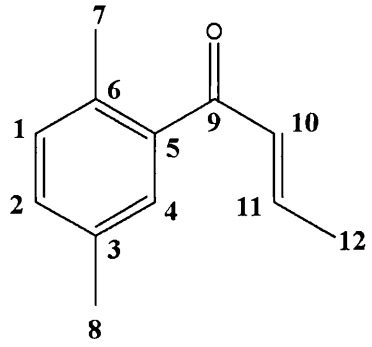
EI m/z (% abundance): 176 (10) [M^+], 161 (3), 143 (5), 133 (100), 115 (10), 105 (63).

1-(2,5-Dimethylphenyl)but-2-en-1-one

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent.



$\delta^{1}H$: 7.22 (1H, s, H^3), 7.14 (1H, d, J = 7 Hz, H^2), 7.0 (1H, d, J = 7 Hz, H^1), 6.63 and 6.67 (1H, 2dq, J = 17 Hz, H^7), 6.40 and 6.44 (1H, 2 separated dd, J = 3, and 1 Hz H^6), 2.41 (3H, s, H^4), 2.37 (3H, s, H^5), 2.0 (3H, d, J = 7 Hz, H^8).



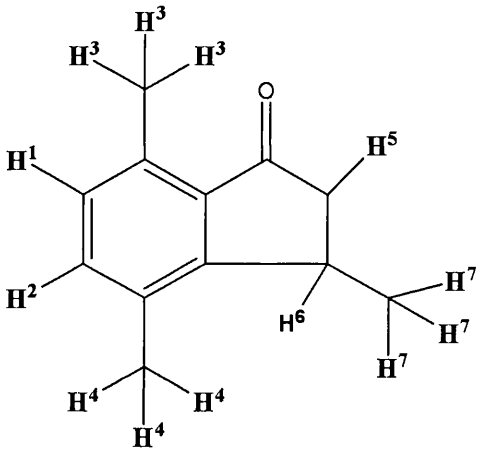
$\delta^{13}C$: 197.6 (C^9), 147.0 (C^4), 139.3 (C^5), 135.2 (C^6), 133.8 (C^3), 132.7 (C^2), 131.4 (C^1), 131.2 (C^{10}), 128.8 (C^{11}), 21.3 (C^7), 20.0 (C^8), 18.9 (C^{12}).

MS:

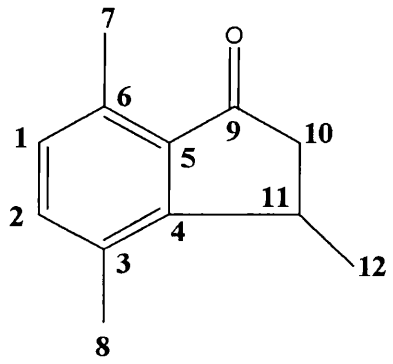
EI m/z (% abundance): 174 (100) [M^+], 158 (10), 132 (14), 122 (5), 104 (3).

3,4,7-Trimethyl-1-indanone

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent.



$\delta^{1}H$: 7.32 (1H, d, J = 7 Hz, H^2), 6.94 (1H, d, J = 7 Hz, H^1), 3.43 (1H, m, H^6), 2.81 (1H, d, J = 7 Hz, H^{5a}), 2.89 (1H, d, J = 7 Hz, $H5^b$) 2.61 (3H, s, H^3), 2.32 (3H, s, H^4), 1.37 (3H, d, J = 7 Hz, H^7).



$\delta^{13}C$: 207.0 (C^9), 135.0 (C^5), 134.4 (C^4), 132.3 (C^6), 131.9 (C^3), 129.9 (C^2), 129.8 (C^1), 45.5 (C^{10}), 27.9 (C^7), 22.7 (C^8), 13.0 (C^{11}), 12.8 (C^{12}).

MS:

EI m/z (% abundance): 174 (73) [M^+], 159 (91), 133 (100), 131 (53), 115 (65), 105 (72).

References

1. R. R. Estes, A. Tockman, *Trans. Kentucky. Acad.*, 13 (1950) 265.
2. C. D. Castro, J. Primo, A Corma, *J. Mol. Catal. A: Chemical.*, 134 (1998) 215.
3. G. A. Olah, *Friedel-Crafts and Related Reactions*, Wiley-Interscience, New York, 1964, vols 1-4.

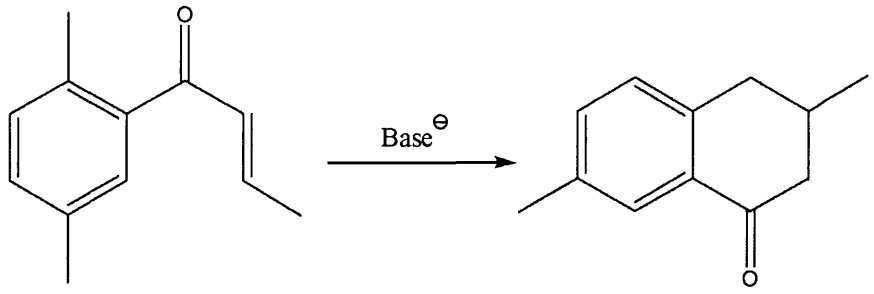
Chapter 2, Part 3

Attempted synthesis of 2,6-dimethyl-1-tetralone

2.3.1 Introduction

In Part 2 of this Chapter (**Section 2.2.4.7**) an optimum 88 % yield of 1-(2,5-dimethylphenyl)but-2-en-1-one was observed in the absence of indanone side product, under optimised reaction conditions. This was achieved when crotonyl chloride (10 mmol) was stirred with *p*-xylene (20 mmol) and aluminium chloride (20 mmol) in the presence of DCM (25 ml) for 180 min, with the reaction mixture being cooled in an ice bath for the initial mixing of the reagents and for the first hour of the reaction. The reaction mixture was then stirred at room temperature for the remaining 120 min.

A stock of pure 1-(2,5-dimethylphenyl)but-2-en-1-one was obtained, allowing the second stage in the synthesis of 2,6-DMN to be investigated. This section of work focuses on the base catalysed reaction of 1-(2,5-dimethyl-phenyl-but-2-en-1-one, in an attempt to produce 2,6-dimethyl-1-tetralone (**Reaction Scheme 2.3.1**). If pure 2,6-dimethyl-1-tetralone is produced in a reasonable yield, the final step in producing 2,6-DMN (aromatisation) can also be investigated.

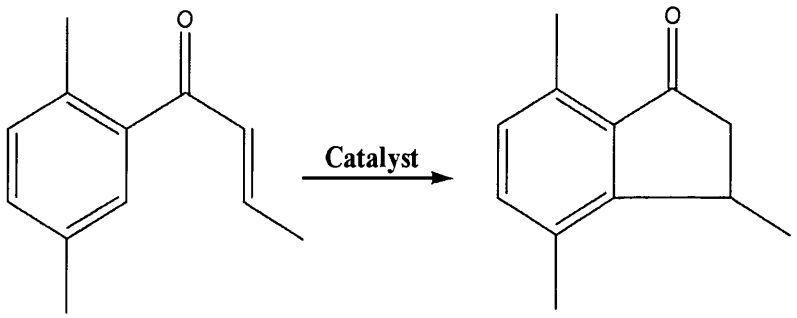


1-(2,5-Dimethylphenyl)but-2-en-1-one **2,6-Dimethyl-1-tetralone**

Reaction Scheme 2.3.1: Base catalysed reaction of the aromatic ketone to give the corresponding tetralone product.

It was reported previously in Part 2 of this chapter that 1-(2,5-dimethylphenyl)but-2-en-1-one had a tendency to undergo an intramolecular

alkylation reaction when an acid catalyst was employed, especially under forcing conditions to yield an indanone side product (**Reaction Scheme 2.3.2**). It was hoped that the isomeric tetralone might be formed under basic conditions.

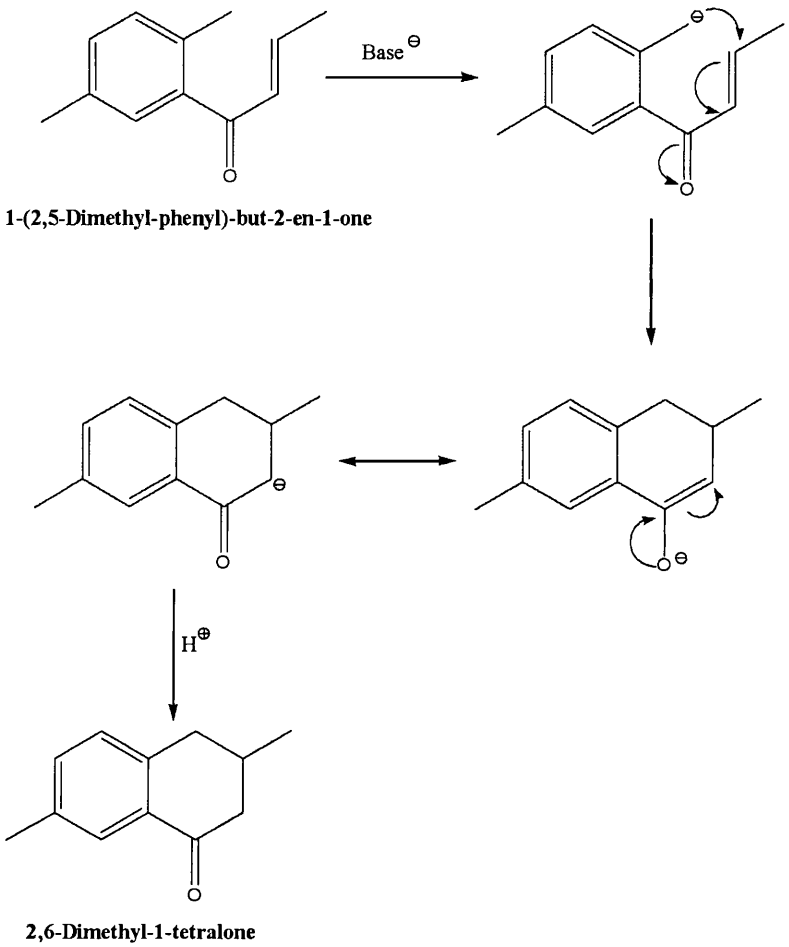


1-(2,5-Dimethylphenyl)but-2-en-1-one **3,4,7-Trimethyl-1-indanone**

Reaction Scheme 2.3.2: Intramolecular alkylation of the aromatic ketone generating the undesirable indanone side product.

2.3.2 Base catalysed reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one

It was hoped that under basic conditions deprotonation of the terminal methyl group (which should be somewhat acidic, though not the most acidic proton) would occur and encourage a cyclisation reaction to give the corresponding tetralone product. A suggested mechanism for this reaction is given in **Reaction Scheme 2.3.3**. Removal of the most acidic terminal proton of the enone system would almost certainly occur preferentially, but might not lead to further reaction. Therefore, it was hoped that the reaction could be encouraged to bleed through the process in reaction scheme 2.3.3 instead. If it were successful, treatment with base would first deprotonate the terminal methyl group of the aromatic ketone to generate a carbanion. Nucleophilic attack of the carbanion on the carbon in the position *beta* to the carbonyl group would result in a cyclisation reaction to give a six membered ring with enolate functionality. The new bicyclic compound would have methyl groups in the desired 2 and 6 positions. On protonation, 2,6-dimethyl-1-tetralone would be `generated.



Reaction Scheme 2.3.3: Suggested reaction mechanism for the cyclisation of 1-(2,5-dimethylphenyl)but-2-en-1-one) under basic conditions, to generate 2,6-dimethyl-1-tetralone.

2.3.3 Attempted synthesis of 2,6-dimethyl-1-tetralone

The base catalysed reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one was carried out with lithium diisopropylamide (LDA) and sodium methoxide (NaOMe). Each of these reactions will be discussed in turn in the following sections.

2.3.4 Reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one with LDA

A solution of 1-(2,5-dimethylphenyl)but-2-en-1-one (0.50 g, 2.8 mmol) in dry THF (50 ml) was added over 20 min to LDA (0.30 g, 2.8 mmol) covered with dry THF (50 ml). The solution was stirred for 3 h at room temperature, under inert atmosphere. The reaction was quenched with saturated sodium chloride solution (50 ml) and the aqueous layer was extracted with diethyl ether (3 x 25 ml) then

washed with water (2 x 25 ml). The organic fractions were combined and dried over magnesium sulphate. Solvents were removed at the pump to yield a residual oil (0.49 g).

GC analysis of the residual oil showed a single peak corresponding to the starting material. NMR and mass spectra were also identical to those of the starting material. It was therefore clear that no reaction had taken place under these conditions, and the starting material was recovered quantitatively.

In view of this, it was decided to carry out a reaction where the reaction mixture was refluxed for three hours in an attempt to generate the desired tetralone product. The reaction was carried out using the same procedure as described above, except for the higher reaction temperature. GC analysis showed once again that the starting material was recovered unreacted (quantitatively).

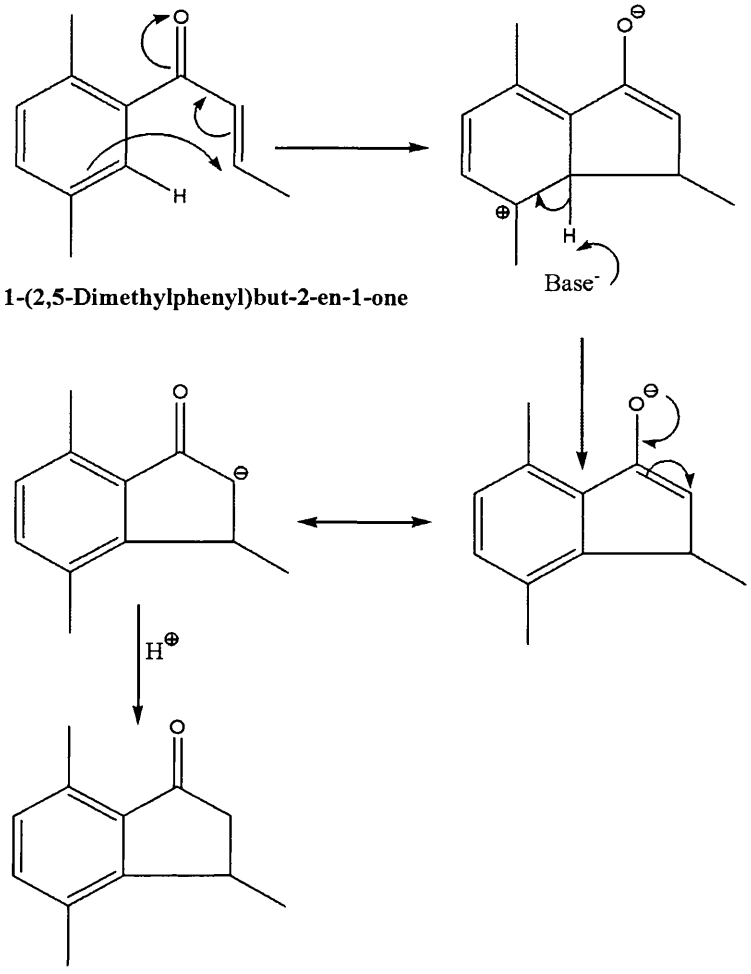
Further reactions were carried out using the procedure described above where the reaction mixture was refluxed for 12 h with both 1 and 2 equivalents of catalyst. GC analysis of the residual oils after the work up of the reaction showed that the desired reaction had not taken place, and once more the starting material was recovered unreacted. In conclusion, the desired tetralone product was not observed in the reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one with LDA, even under forcing conditions. It was therefore decided to investigate the reaction with other base catalysts.

2.3.5 Reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one with sodium methoxide

A reaction was carried out using a similar procedure to that described in Section **2.3.4** but with sodium methoxide in methanol as base instead of LDA in THF. A solution of 1-(2,5-dimethylphenyl)but-2-en-1-one (0.50 g, 2.8 mmol) in methanol

(50 ml) was added over 20 min to NaOMe (0.15 g, 2.8 mmol) covered with methanol (50 ml). The solution was refluxed for 3 h at room temperature, under inert atmosphere. The reaction was quenched with water (50 ml) and a residual oil (0.48 g) was obtained after the work up. GC analysis of the crude oil gave three peaks with retention times of 10.63 min, 13.42 min and 14.34 min. The peaks with retention times of 13.42 min and 14.32 min corresponded to unreacted aromatic ketone starting material and 3,4,7-trimethyl-1-indanone, respectively. This was confirmed by co-injection of pure samples of each compound with the crude oil. **Reaction Scheme 2.3.4** gives a suggested reaction mechanism for the formation of 3,4,7-trimethyl-1-indanone from the reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one with sodium methoxide.

Because sodium methoxide is a weaker base than LDA, perhaps some undeprotonated material would remain in the solution. This could cyclise and lose a proton to give the final product.



1-(2,5-Dimethylphenyl)but-2-en-1-one

3,4,7-Trimethyl-1-indanone

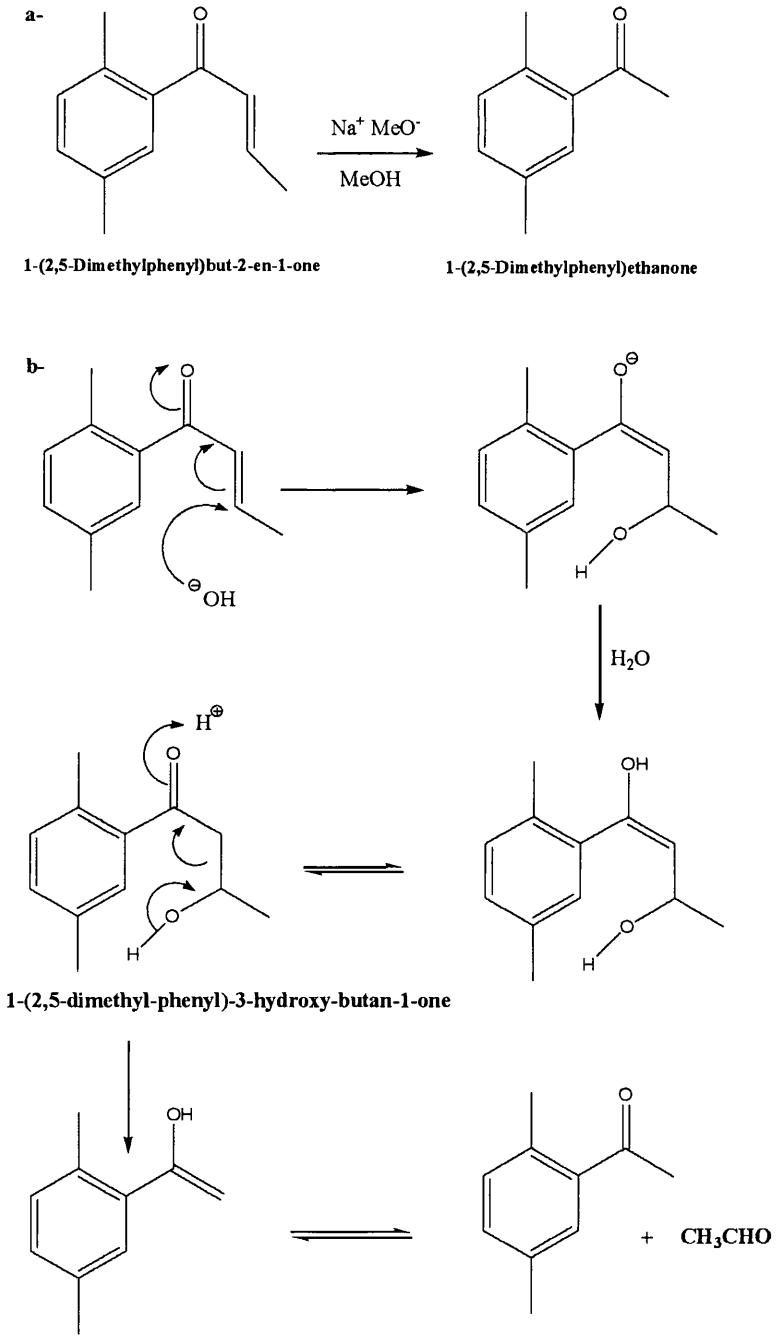
Reaction Scheme 2.3.4: Suggested reaction mechanism for the intramolecular alkylation of the aromatic ring in 1-(2,5-dimethylphenyl)but-2-en-1-one, to generate 3,4,7-trimethyl-1-indanone in basic conditions.

2.3.6 Identification of compound with retention time of 10.63 min.

Separation of the unknown isomer from the crude reaction mixture was attempted several times by reduced pressure distillation and column chromatography, but it was not isolated in pure form.

The crude reaction mixture was subjected to GCMS analysis which showed that the compound with retention time 10.63 min had a relative molecular mass of 148. It was thought that the unknown compound may correspond to 1-(2,5-dimethylphenyl)ethanone, **Reaction Scheme 2.3.5** gives a suggested reaction

mechanism, based on the assumption that there was some water, and therefore hydroxide ion, in the system, leading to the possibility of a retro-aldol reaction.



Reaction Scheme 2.3.5: Suggested reaction mechanism for the production of 1-(2,5-dimethylphenyl)ethanone from a reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one with sodium methoxide and undried methanol.

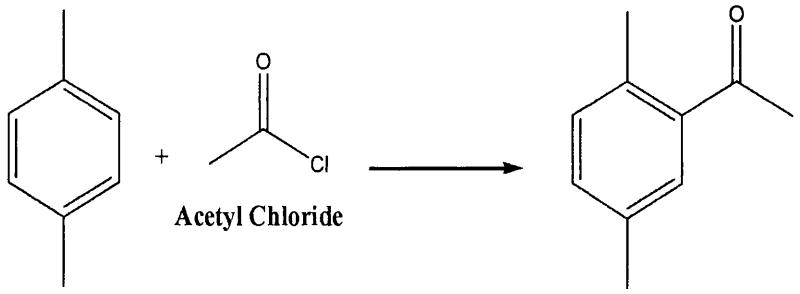
Addition of a hydroxide ion to the carbon in the position *beta* to the carbonyl group via a basic Michael addition is followed by protonation to give a *beta*-hydroxyketone (1-(2,5-dimethylphenyl)-3-hydroxybutan-1-one). This then

undergoes a retro aldol reaction where the hydroxy group is deprotonated, the carbonyl is protonated, and the 2-3 bond is cleaved to give 1-(2,5-dimethyl-phenyl)-ethanone and ethanal.

A pure sample of 1-(2,5-dimethylphenyl)ethanone was not available for co-injection with the crude reaction mixture. Therefore, it was decided to prepare 1-(2,5-dimethylphenyl)ethanone via a known route, in order to determine whether this was the compound generated in the reaction of 1-(2,5-dimethylphenyl)but-2-ene-1-one with sodium methoxide.

2.3.7 Preparation of 1-(2,5-dimethylphenyl)ethanone from *p*-xylene and acetyl chloride catalysed by aluminium chloride

1-(2,5-Dimethylphenyl)-ethanone was synthesised from *p*-xylene and acetyl chloride catalysed by aluminium chloride in a typical Friedel-Crafts acylation reaction, illustrated in **Reaction Scheme 2.3.6** (the reaction mechanism of this reaction is discussed in Section **2.1.6.2** in Part 1 of this Chapter).



Reaction Scheme 2.3.6: Reaction of *p*-xylene and acetyl chloride catalysed by aluminium chloride

The reaction was carried out using the same procedure as described in Section **2.2.6.2** in Part 2 of this Chapter. Acetyl chloride (0.78 g, 10 mmol) was stirred in an excess of *p*-xylene (36.8 g, 347 mmol) with two equivalents of aluminium chloride

(1.27 g, 20 mmol), at room temperature for 3 h under an inert atmosphere. The reaction was quenched by addition of 2 M $NaHCO_3$ solution, and the solid formed was filtered at the pump. The filtrate was separated into two layers and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and dried over magnesium sulfate. Solvents were evaporated at the pump and *p*-xylene was removed by reduced pressure distillation, to afford the acylated product in a 63 % yield. Purity was checked by GC and the structure of 1-(2,5-dimethylphenyl)ethanone was confirmed by NMR and MS analysis.

A pure sample of 1-(2,5-dimethylphenyl)ethanone was co-injected with the crude reaction mixture which confirmed that the unknown compound with retention time 10.63 min corresponded to 1-(2,5-dimethylphenyl)ethanone.

One can conclude that in the reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one with sodium methoxide the desired 2,6-dimethyl-1-tetralone product was not observed. The major product observed was 3,4,7-trimethyl-1-indanone, resulting from an intramolecular alkylation reaction. 1-(2,5-Dimethylphenyl)ethanone was also observed, via a mechanism which was thought to involve a Michael addition reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one to give 1-(2,5-dimethylphenyl)-3-hydroxybutan-1-one, which then underwent a retro-aldol reaction to give 1-(2,5-dimethylphenyl)ethanone.

2.3.8 Summary and conclusions

The synthesis of 2,6-dimethyl-1-tetralone was attempted by reacting 1-(2,5-dimethylphenyl)but-2-en-1-one with LDA and sodium methoxide. In the reaction with LDA no reaction took place even under forcing conditions, and the starting material was recovered quantitatively.

In the reaction with sodium methoxide, an intramolecular alkylation reaction took place to give 3,4,7-trimethyl-1-indanone as the major product. 1-(2,5-dimethylphenyl)ethanone and 1-(2,5-dimethylphenyl)but-2-en-1-one were also observed. The desired 2,6-dimethyl-1-tetralone was not observed.

The base catalysed reaction of 1-(2,5-dimethylphenyl)but-2-en-1-one was not pursued any further due to time constraints and the unencouraging results to date.

2.3.9 Focusing on a different route to prepare an analogue of 2,6-DMN to be used in the production of PEN

In addition to the unsuccessful production of the tetralone in the second step of the synthesis of 2,6-DMN, the zeolite catalysed synthesis of the aromatic ketone starting material from *p*-xylene and crotonic acid was also unsuccessful (Part 1 of this Chapter). In view of this, it was decided to investigate a different route to produce an analogue of 2,6-DMN, for use in the production of PEN. This involves the direct reaction of the naphthalene ring. This will be discussed at length in the following Chapters.

2.3.9 Experimental

General experimental

All instrumentation, analytical methods and reagents employed are included as an appendix.

Stirring of the reaction mixtures was achieved by means of a magnetic stirrer and an internal magnetic follower. Heating of reaction mixtures was achieved by a hot-plate and an oil bath. The temperature of the oil bath was controlled by a contact thermometer.

2.3.9.1 Attempted synthesis of 2,6-dimethyl-1-tetralone with LDA

A solution of 1-(2,5-dimethylphenyl)but-2-en-1-one (0.50 g, 2.8 mmol) in dry THF (50 ml) was added over 20 min to LDA (0.30 g, 2.8 mmol) covered with dry THF (50 ml) in a 200 ml double necked round bottomed flask fitted with a magnetic stirrer bar, dropping funnel and reflux condenser. The solution was stirred under reflux for 3 h under argon. The reaction was quenched with saturated sodium chloride solution (50 ml) and the mixture was separated into organic and aqueous layers. The aqueous layer was extracted with diethyl ether (3 x 25 ml) and combined organic extracts were then washed with water (2 x 25 ml). The organic layer was dried over magnesium sulfate. Solvents were removed at the pump to yield a residual oil (0.49 g) (corresponding to unreacted starting material).

2.3.9.2 Attempted synthesis of 2,6-dimethyl-1-tetralone with sodium methoxide

A solution of 1-(2,5-dimethylphenyl)but-2-en-1-one (0.50 g, 2.8 mmol) in methanol (50 ml) was added over 20 min to NaOMe (0.15 g, 2.8 mmol) covered with methanol (50 ml) in a 200 ml double necked round bottomed flask fitted with a magnetic stirrer bar, dropping funnel and reflux condenser. The solution was stirred under reflux for 3 h under nitrogen. The reaction was quenched with water (50 ml)

and the mixture was separated into organic and aqueous layers. The aqueous layer was extracted with diethyl ether (3 x 25 ml) and combined organic extracts were then washed with water (2 x 25 ml). The organic layer was dried over magnesium sulfate. Solvents were removed at the pump to yield a residual oil (0.48 g). GC analysis of the crude oil gave three peaks with retention times of 10.63 min, 13.42 min and 14.34 min corresponding 1-(2,5-dimethylphenyl)ethanone, unreacted aromatic ketone starting material and 3,4,7-trimethyl-1-indanone, respectively. This was confirmed by co-injection of pure samples of each compound with the crude oil.

2.3.9.3 Synthesis of 1-(2,5-dimethylphenyl)ethanone

A solution of acetyl chloride (0.78 g, 10 mmol) and *p*-xylene (2.14 g, 20 mmol) was added drop-wise over 20 min to aluminium chloride (1.27 g, 20 mmol) covered with *p*-xylene (34.7 g, 327 mmol) in a 200 ml double necked round bottomed flask fitted with a magnetic stirrer bar and a dropping funnel.

The solution was stirred for 3 h under argon, at room temperature. After the given reaction time the reaction was quenched with 2 M $NaHCO_3$ solution (100 ml) and the solid formed was filtered at the pump. The filtrate was separated and the aqueous layer was extracted with diethyl ether (3 x 25 ml). The combined organic extracts were washed with water (2 x 25 ml) and then dried over magnesium sulfate. Solvents were evaporated at the pump and *p*-xylene was removed by reduced pressure distillation to afford the acylated product (0.93 g) in a 63 % yield.

2.3.10 GC analysis

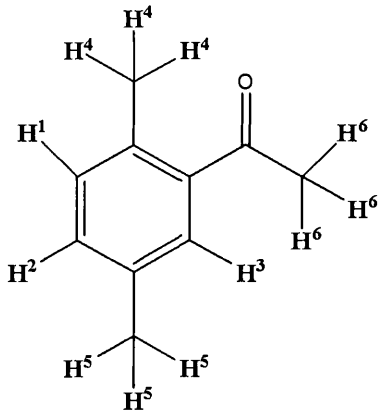
GC analysis of product mixtures was carried out using the same conditions as set out in Section **2.1.13** in Part 1 of this Chapter. The GC traces of the product mixtures from reactionss of 1-(2,5-dimethylphenyl)but-2-en-1-one with LDA gave one peak with retention time 13.42 min, corresponding to the starting material. The

GC traces of the product mixtures from the reaction of 1-(2,5-dimethlphenyl)but-2-en-1-one with sodium methoxide gave three peaks with retention times of 10.63 min, 13.42 min and 14.34 min corresponding to 1-(2,5-dimethylphenyl)ethanone, 1-(2,5-dimethylphenyl-but-2-en-1-one and 3,4,7-trimethyl-1-indanone, respectively.

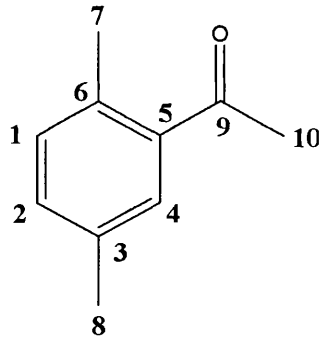
2.3.11 Analytical data

1-(2,5-Dimethyl-phenyl)-ethanone

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent.



$\delta^{1}H$: 7.4 (1H, s, H^3), 7.2 (1H, d, J = 7 Hz, H^2), 7.1 (1H, d, J = 7 Hz, H^1), 2.5 (3H, s, H^4), 2.3 (3H, s, H^5), 2.2 (3H, s, H^6).



$\delta^{13}C$: 202.4 (C^9), 138.0 (C^5), 135.6 (C^3), 135.6 (C^6), 132.6 (C^4), 132.3 (C^2), 130.3 (C^1), 30.1 (C^{10}), 21.5 (C^7), 21.3 (C^8).

MS:

EI m/z (% abundance): 148 (48) [M^+], 142 (15), 134 (20), 133 (100), 121 (18).

Chapter 3, Part 1

Initial Alkoxyalkylation of Naphthalene

3.1.1 Introduction

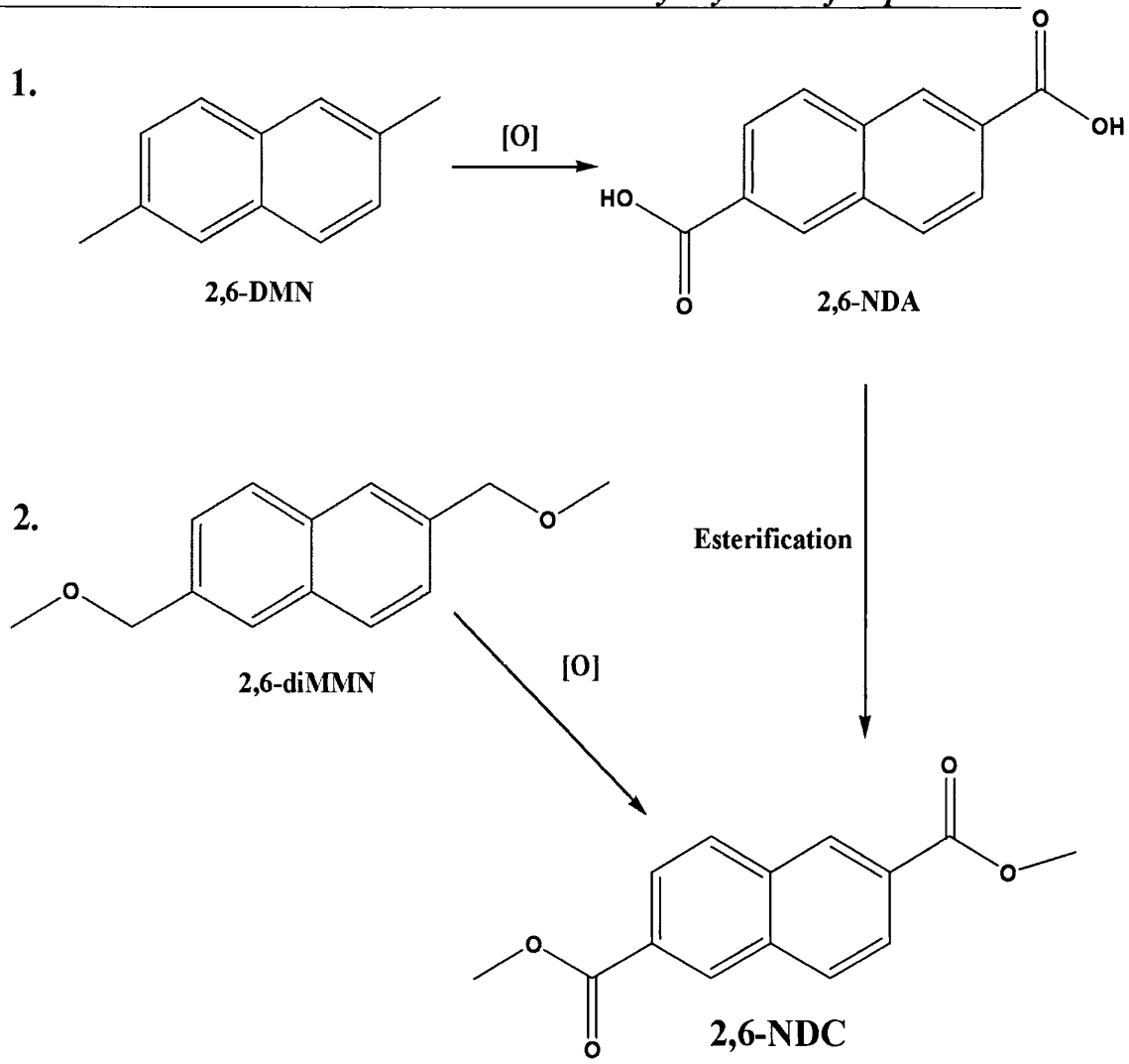
The synthesis of 2,6-DMN from *p*-xylene and crotonyl chloride (discussed in Chapter 2) was attempted with little success. This was because the major product generated from the second base catalysed step of the reaction, was an undesirable side product containing a 5-membered ring, rather than the desired tetralone intermediate. Therefore, 2,6-DMN could not be generated. Thus a superior method was still required for producing a precursor for 2,6-NDC for use in the synthesis of PEN, from cheap, readily available starting materials using the minimum number of steps with green catalysts (zeolites).

3.1.2 An alternative route

Zeolite catalysed substitution reactions of benzene and its derivatives (phenol, toluene, chlorobenzene etc) have been well documented in the literature[1] and were discussed briefly in Chapter 1. In contrast, much less consideration has been paid regarding the substitution reactions of bulkier polycyclic aromatics such as naphthalene. It was therefore decided to investigate a process for producing a precursor for 2,6-NDC based on the direct reaction of the naphthalene ring itself.

The synthesis of several 2,6-diaalkylnaphthalenes from the direct alkylation of naphthalene, over various zeolites was discussed extensively in chapter 1. It was shown that the route was limited, both in terms of the yield of the desired product and the selectivity of the reaction towards the 2,6 isomer.

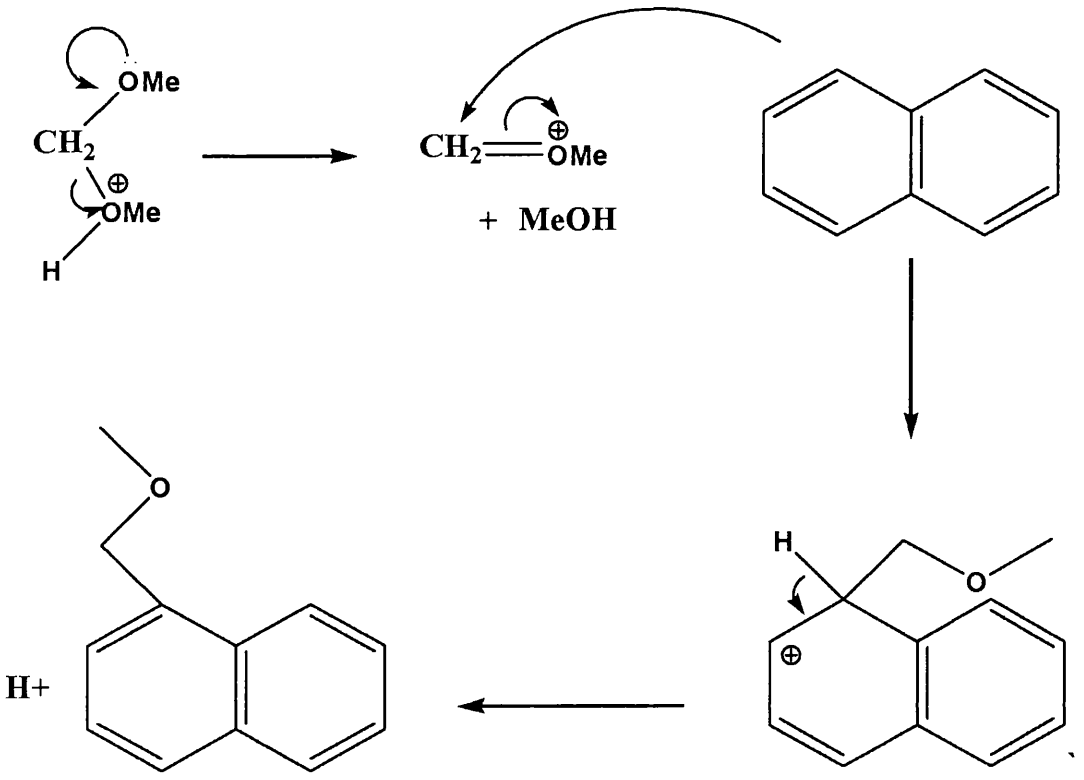
It was thought that this method could be improved by introducing an alkoxy functionality to the substituent. The inclusion of an oxygen atom could eliminate an oxidation step in the production of PEN (**Reaction scheme 3.1.1**).



Reaction scheme 3.1.1: Comparison of bis(methoxymethyl)naphthalene and dimethylnaphthalene as precursors for 2,6-NDC.

It is industrially favourable, both in terms of the economics and time scale of the process if the number of steps required to get to the final product is reduced.

The alkoxyalkylation of naphthalene or aromatic compounds in general has not been well documented in the literature. This chapter is concerned with the alkoxyalkylation of naphthalene with dimethoxymethane (DMM) and diethoxymethane (DEM) as alkoxyalkylating agents, to generate (methoxymethyl)naphthalene (MMN) and (ethoxymethyl)naphthalene (EMN), respectively via a basic electrophilic aromatic substitution pathway (**Reaction scheme 3.1.2**).



Reaction scheme 3.1.2: Reaction mechanism for the methoxymethylation of naphthalene

Reaction scheme 3.1.2 illustrates how dimethoxymethane is protonated on treatment with an acidic catalyst to generate an electrophile which attacks the naphthalene ring. The electrophile forms a sigma bond to the naphthalene ring generating a positively charged naphthenonium intermediate; a proton is then lost from this intermediate yielding a substituted naphthalene ring and restoring the aromaticity.

As mentioned in Chapter 1, there are 10 possible isomers of bis(MM)N and bis(EM)N that could be produced and it was paramount that the reaction was selective towards the 2,6-disubstituted isomers. Therefore, zeolite catalysts were employed because they exhibit shape selectivity.

Both 2,6-bis(MM)N and 2,6-bis(EM)N would ultimately give the same PEN product. The only difference would be a loss of MeOH or EtOH, respectively in the final transesterification step with ethylene glycol.

In order to understand the reaction in more detail the next section introduces naphthalene, and the main principles of electrophilic substitution reactions.

3.1.3 Naphthalene

Naphthalene is the smallest known polycyclic aromatic compound. It comprises two benzene rings which are fused together and share two common carbon atoms *ortho to* each other (**Figure 3.1.1**). The naphthalene ring is numbered as shown in figure 3.1 where positions 1, 4, 5 and 8 are equal and are often referred to as the 'α'positions. Positions 2, 3, 6 and 7 are also equal and are often referred to as the 'β' positions. Naphthalene is a natural component of fossil fuels and can be obtained from coal tar (by- product of the coking of coal) and petroleum. Since 1960 the recovery of naphthalene from petroleum by dealkylation of methylnaphthalenes in the presence of hydrogen at high temperature and pressure has been a commercial production process[1].

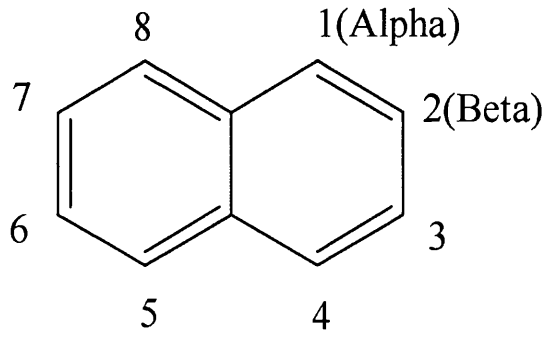


Figure 3.1.1: Structure and numbering of naphthalene

Naphthalene exhibits similar chemical stability to benzene and as with monocyclic aromatic compounds, polycyclic aromatic compounds have several important resonance contributors. The two fused benzene rings of naphthalene are not both benzenoid at the same time and can be represented as a resonance hybrid (**Figure 3.1.2**). The two structures on the left have one discrete benzene ring each, but may

also be viewed as 10 pi-electron annulenes having a bridging single bond. The structure on the right has two benzene rings which share a common double bond.

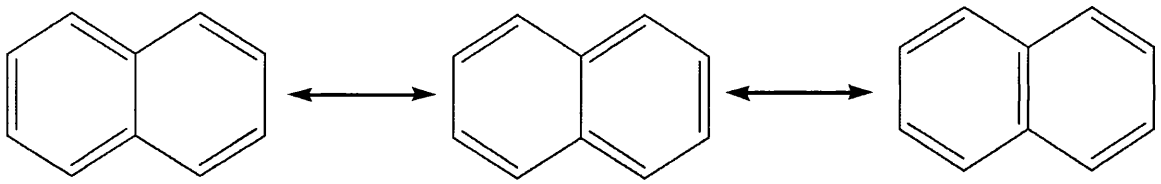


Figure 3.1.2: Resonance hybrids of naphthalene

From an average of the three resonance contributors the C-C bonds in naphthalene are not equal which suggests localisation of the double bonds. The C1-C2 bond is 136 pm long compared to the C2-C3 bond length which is 140 pm **(Figure 3.1.3)**[2]. This contrasts with the structure of benzene, in which all the C-C bonds have a common length, 139 pm.

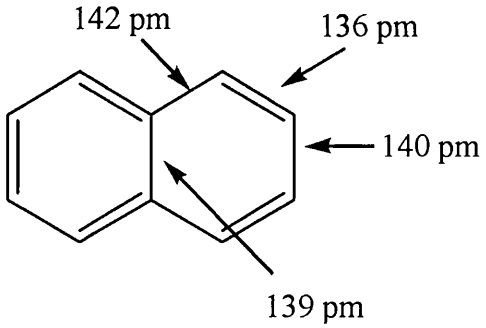


Figure 3.1.3: Different bond lengths within the naphthalene ring

3.1.4 Electrophilic aromatic substitution reactions of naphthalene

Naphthalene reacts with similar reagents to benzene but is typically more reactive both in substitution and addition reactions, and these reactions tend to proceed in a manner that maintains one intact benzene ring. Electrophilic aromatic substitution reactions are probably the most commercially significant class of reactions of naphthalene and allow the introduction of substituents onto the naphthalene ring. These reactions have been well documented in the literature and include sulfonation, alkylation, nitration and chlorination.

Under reaction conditions that favour kinetic control naphthalene undergoes electrophilic substitution reactions more rapidly at the α position. This can be understood in terms of the naphthenonium ion that is generated which requires a lower energy and is therefore more stable than the naphthenonium ion generated, from attack of an electrophile at the β position. The kinetically favoured α orientation reflects a preference for generating a cationic intermediate that maintains one intact benzene ring. Two canonical forms can be written for α substitution where the second ring remains benzenoid (such canonical forms have lower energies than when both π systems are disrupted). This is not true for attack at the β position, where there is only one canonical form in which the second ring remains benzenoid (**Figure 3.1.4**). In contrast, the isomer generated from β substitution is more thermodynamically stable and predominates if the reaction is reversible and reaches equilibrium.

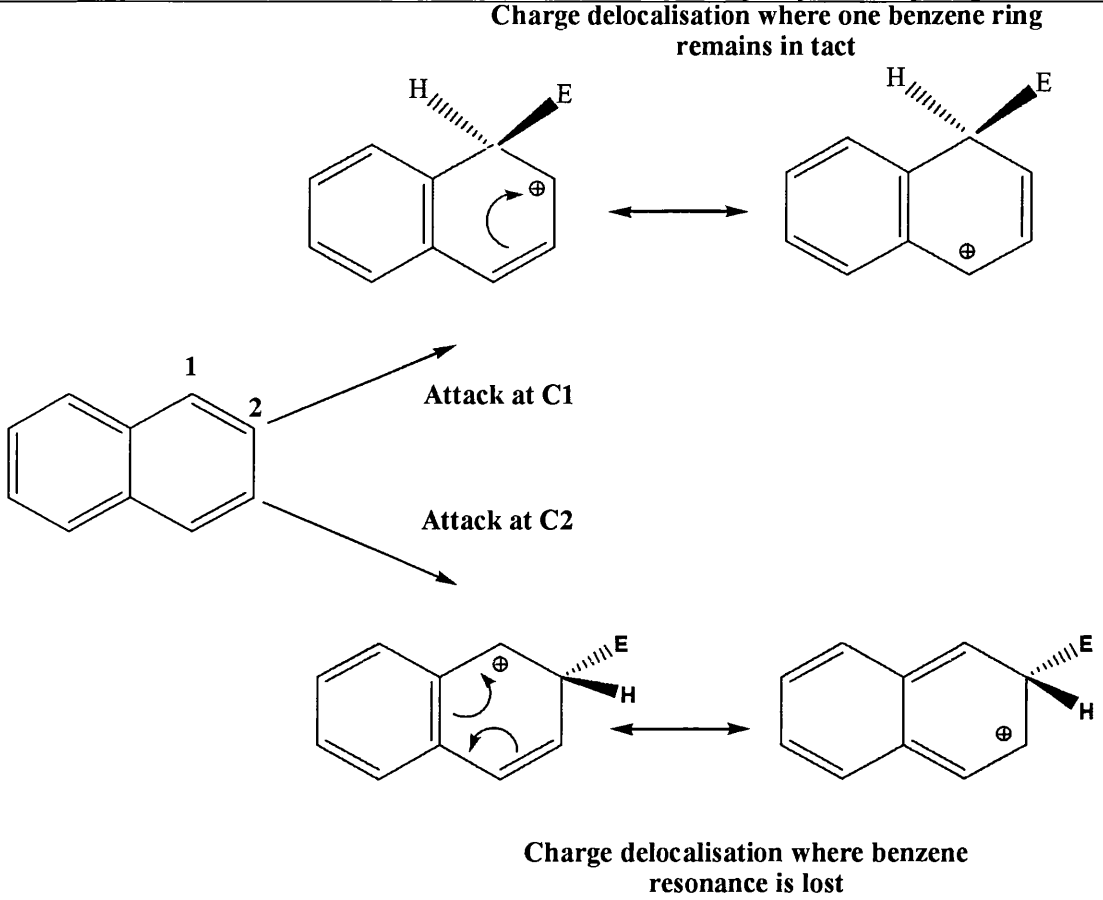


Figure 3.1.4: Naphthenonium intermediates created by attack at C1 and C2

The sulfonation of naphthalene is a reaction which illustrates thermodynamic versus kinetic control. Naphthalene-1-sufonic acid is the major product observed (98 % yield) with sulfuric acid when the reaction temperature is less than 75 °C. Conversely, if the reaction temperature is increased above 165 °C (or if naphthalene-1-sulfonic acid is heated above 165 °C in sulphuric acid) naphthalene-2-sulfonic acid is the major product and is observed in an 88 % yield[3].

When the naphthalene substituent is bulky isomerisation between the α and β positions is commonly observed and β substitution is favoured if the substituent is large. This is because the fused benzene ring structure of naphthalene creates steric

hindrance between positions 1 and 8. A reaction which exhibits this phenomenon is the sulfonation of naphthalene (**Figure 3.1.5**).

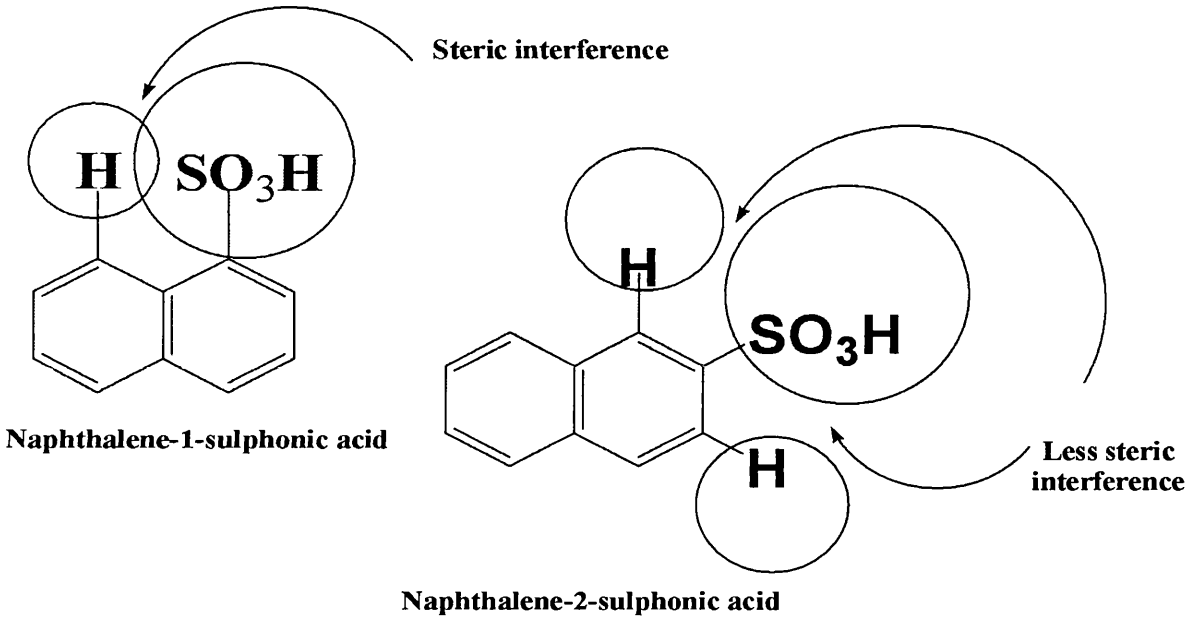


Figure 3.1.5: α Substitution favoured with bulky substituents due to steric hindrance

When the bulky sulfonic acid group is attatched at the α (C1) position it comes within the Van de Waals radius of the hydrogen at C8. No such steric hindrance is observed when the sulfonic acid group is attatched at the β position (C2) because the molecule has sufficient room for the sufonic acid group between the hydrogens at C1 and C2. Consequently, the product of the higher energy pathway is actually more stable than the product of the lower energy pathway.

There are certain rules of activation and deactivation regarding the effect of particular substituents on further electrophilic attack which apply to benzene and naphthalene alike (with regards to naphthalene even though the effect of a substituent in a fused ring system affects both rings, the effect is generally greatest on the ring

which is substituted). If the initial substituent is electron-withdrawing then further electrophilic attack is directed into the unsubstituted benzene ring. Conversely, the opposite is true when the initial substituent is electron-donating.

3.1.5 Initial results of the methoxymethylation of naphthalene

3.1.5.1 Investigating various types of zeolites

An initial set of experiments was carried out where several different zeolites* were employed to catalyse the reaction between dimethoxymethane and naphthalene, in an attempt to determine which zeolite was most active in terms of (methoxymethyl)naphthalene formation and which was most selective towards the favoured 2 isomer. Each experiment was carried out under identical reaction conditions in a stirred mini reactor at 150 °C for 18 h under self generated pressure with dimethoxymethane (80 mmol), naphthalene (10 mmol), cyclohexane (60 ml) and various zeolites (4 g).

* Zeolites employed in the preliminary reactions included: Protonated Zeolite Y (**HY**), sodium exchanged Zeolite Y (**NaY**), protonated Zeolite Mordenite (**HM**), sodium exchanged Zeolite Mordenite (**NaM**), protonated Zeolite Beta (**HBeta, Hβ**), sodium exchanged Zeolite Beta (**NaBeta, Naβ**) and protonated Zeolite ZSM-5 (**HZSM-5**).

3.1.5.2 Presentation of results

The mol % recovery of naphthalene, mol % yield of methylnaphthalene (2 isomers detected), mol % yield of (methoxymethyl)naphthalene (2 isomers detected), 2/1 ratio, mol % yield of bis(methoxymethyl)naphthalene (3 isomers detected), mol % yield of methylenebis(naphthalene) (3 isomers detected) and total mol % are presented.

The proportions of recovered naphthalene and products formed were determined from calculations based on GC analysis. Numbers are expressed as percentages and have been rounded to the nearest whole number, except numbers that are < 1 which are expressed to 1 decimal place.

The 2/1 ratio corresponds to the ratio of the 1 and 2 isomers of (methoxymethyl)naphthalene. This ratio was determined by a direct comparison of GC peak areas.

The Swansea experiment code corresponds to the code of each reaction carried out in the lab in Swansea. It is included for my own convenience not intended for the purpose of the thesis reader.

Table 3.1.1: The effect of different zeolites on reactions between naphthalene and dimethoxymethane[a].

Catalyst	HY	NaY	NaM	HM	HBeta	NaBeta	HZSM-5
Si/Al ratio	15	2.8	15	20	25	25	75
Swansea experiment code	D1	D3	D5	D7	D9	D11	D13
Naphthalene recovery (%)	32	98	97	87	45	54	98
Methylnaphthalenes (%)	2	0	0	5	3	2	0
MMN (%)	3	0	0	4	19	18	0
2/1 ratio	0.4	_	_	12.9	1.9	1.6	_
bis(MM)N (%)	0	0	0	0	6	5	0
MBN (%)	50	0	0	0	0	0	0
Total (%)	87	98	97	96	73	79	98

[a] 18 h stirred mini reactor reactions at 150 °C under self generated pressure; catalyst (4 g), naphthalene (1.28 g, 10 mmol), dimethoxymethane (6.08 g, 80 mmol) and cyclohexane as solvent (60 ml)

The results in Table 3.1.1 show how the yield and selectivity of the products formed varied significantly over different types of zeolites. In terms of selectivity HM was the most promising zeolite; a 2/1 ratio of 12.9 was achieved. The high selectivity observed with HM can be explained in terms of the channels within the zeolite framework, which are long cylindrical channels that would allow the movement of the 2 isomer more readily than the 1 isomer. This is because it has a narrower cross

section (example of shape selectivity and steric interference described at the beginning of the Chapter).

Unfortunately the high selectivity was not coupled with a high yield of MMN where a 4 % yield was observed together with a 5 % yield of methylnaphthalene.

In principle, methylnaphthalene could have been generated either from direct methylation with MeOH (produced from dimethoxymethane on treatment with the acid catalyst), or from the degradation of the product itself MMN. The latter is more unlikely since a source of hydride ions (H^-) would be required. It was more probable that it was produced by methylation of naphthalene with MeOH.

HY was found to be the most active zeolite where a 68 % conversion of naphthalene was achieved. The major product comprised 3 isomers of methylenebis(naphthalene) (50 % yield). Methylenebis(naphthalene) (MBN) is an undesirable side product that incorporates two molecules of naphthalene, bridged by a methyl group. It was thought it was formed by reaction of mono(methoxymethyl)naphthalene (MMN) with a further molecule of naphthalene in the presence of the acid catalyst. The feasibility of MBN formation over HY can be understood in terms of the structure of HY itself which is a large pore zeolite (7.4 Å in diameter) which would allow the formation of larger products. MMN was detected in a 3 % yield along with 2 % yield of methylnaphthalene.

NaY, NaM and HZSM-5 were the least active zeolites, GC analysis of the reaction mixtures showed no reaction had occurred and naphthalene was recovered quantitatively.

The most encouraging reactions, which gave the highest yields of MMN, were when Hβ and Naβ were employed, where MMN was observed in a 19 % and 18 % yield respectively (methylnaphthalene was also detected in both reactions). GCMS

analysis of the reaction mixture gave three peaks corresponding to compounds with a molecular weight of 216, suggesting the formation of three different isomers of bis(MM)N. The separation of the three isomers was attempted by column chromatography but was unsuccessful at this stage due to the similar physical properties of the compounds. Therefore, it was impossible to decipher whether the desired 2,6- isomer had been generated and in what yield, compared to the other isomers formed. The three isomers were in the ratio of 2:1:6 and were generated in a 6 % yield over Hβ and a 5 % yield over Naβ.

Both 1 and 2 mono(methoxymethyl)naphthalene products were generated over Hβ and Naβ, so it was conceivable that the disubstituted isomers formed could have been any of the 10 possible isomers (1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,7- and the desired 2,6- isomer) given that a second substitution could have taken place on the first or second ring (see **Figure 1.3.3** in Part 3 of Chapter 1 regarding regioselective alkylation of naphthalene). The structure determination of the disubstituted isomers will be discussed at length in Part 3 of this Chapter.

Although Hβ and Naβ were fairly active, generating both mono and bis(MM)N, the reactions were limited in terms of their selectivity towards the favoured 2 isomer and a 2/1 ratio of less than 2 was achieved in both cases.

3.1.5.3 Limitations associated with low recovery of material

The major limitation associated with the reactions catalysed by Hβ and Naβ was the low recovery of material from the reaction mixture, where almost 25 % of material was unaccounted for. Hβ and Naβ were the only zeolites that generated the di-substituted compounds, and one can speculate that tri or poly substituted naphthalene compounds in addition to various bridged compounds may also have

been generated. If this were the case, then conceivably these bulky compounds could have been trapped within the zeolite framework, unable to exit. These heavy secondary products, designated as coke, can poison the active sites or block their access. It has been well documented that the coking of zeolites can occur with reactions of polycyclic compounds[4-5], where the material is non retractable from the zeolite, even when extracted with solvent for extended periods of time. Consequently, a low product yield recovery of material is observed.

To establish whether coking was responsible for the low recovery observed in these reactions, the spent zeolite catalysts were analysed. As part of the work up of the reactions the zeolites had been washed with acetone during the filtration of the reaction mixture. They were extracted again with acetone (2 x 100 ml) (where the zeolites were stirred in acetone for 1 h) however, no further compounds were extracted. The zeolites were then dried over P_2O_5 for 24 h. The spent zeolites were weighed and it was found that they had incorporated an extra 0.50 g of material during the reaction, which is evidence that non-extractable material had been retained by the zeolite.

3.1.5.4 Treatment of spent zeolites with HF

The spent zeolite (4.50 g) was treated with aqueous HF (30 ml, 40 %) until it dissolved completely; 1 M aqueous sodium hydroxide (100 ml) was then added. Solid NaF was filtered at the pump and the resultant solution was extracted with ether (6 x 30 ml) and washed with water (2 x 30 ml). The organic fractions were combined and dried over $MgSO_4$. Solvents were removed at the pump to give a brown residue (0.47 g), which did not give any peaks on GC analysis. This indicated that the material was not volatile.

The residue was distilled under reduced pressure using kugelrorh distillation apparatus and a yellow crystalline material was isolated (again, no peaks on GC analysis). NMR of the brown residue and yellow solid were carried out and the NMR spectra were very complicated. Numerous signals were observed in the aromatic and aliphatic regions which may correspond to naphthalene derivatives. The effect of coke on the catalytic activity of the zeolite will be discussed in Part 2 of this Chapter.

3.1.6 Ethoxymethylation of naphthalene

3.1.6.1 Investigating various types of zeolites

An analogous set of experiments was carried out with diethoxymethane as the alkoxyalkylating reagent to determine if the selectivity of the reactions would be better than with dimethoxymethane.

Each experiment was carried out under identical reaction conditions in a stirred mini reactor at 150 °C for 18 h under self generated pressure with diethoxymethane (80 mmol), naphthalene (10 mmol), cyclohexane (60 ml) and various zeolites (4 g). Several products were identified by GC/MS in several product mixtures, including (ethoxymethyl)naphthalenes (2 isomers), methylnaphthalenes (2 isomers) and unreacted naphthalene. There were even traces of (methoxymethyl)naphthalenes in some cases.

3.1.6.2 Presentation of results

The mol % recovery of naphthalene, mol % yield of methylnaphthalenes, mol % yield of (ethoxymethyl)naphthalenes, 2/1 ratio of the (ethoxymethyl)naphthalenes and total mol % (i.e. the sum of the yields of the identified products) are presented.

The 2/1 ratio corresponds to the ratio of the 2-substituted and 1-substituted isomers of (ethoxymethyl)naphthalene. This ratio was determined by a direct comparison of GC peak areas.

Table 3.1.2: Effect of different zeolites on reactions between naphthalene and diethoxymethane[a].

Catalyst	HY	NaY	NaM	HM	Hbeta	NaBeta	HZSM-5
Si/Al ratio	15	2.8	15	20	25	25	75
Swansea experiment code	D2	D4	D6	D8	D10	D12	D14
Naphthalene conversion (%)[b]	9	6	1	47	15	3	12
Naphthalene recovery (%)[b]	91	94	99	53	85	97	88
Methylnaphthalenes (%)[b]	0	0	0	2	0	0	4
EMN (%)[b]	3*	4	0	33	11*	1	6
2/1 ratio[c]	0.6	0.3	_	1.9	0.4	1.7	2.1
Total (%)[b]	94	98	99	88	96	98	98

[a] 18 h stirred mini reactor reactions at 150 °C under self generated pressure; catalyst (4 g), naphthalene (1.28 g, 10 mmol), diethoxymethane (8.32 g, 80 mmol) and cyclohexane as solvent (60 ml).
* Small amounts of 1 and 2-(methoxymethyl)naphthalenes also present in the crude mixture.

The results presented in Table 3.1.2 show how NaY, Naβ, HZSM-5 and HY were comparable in terms of poor activity and selectivity; it was also noted that the undesirable side product MBN was not generated with HY, although it had been formed in high yield in the reaction with dimethoxymethane.

In addition to the formation of EMN, trace amounts of MMN were also generated when HY and Hβ were employed. It was not clear how MMN was generated but one can speculate that some kind of degradation reaction of EMN took place. As mentioned earlier a mixture of MMN and EMN would not affect the purity of PEN, the only difference would be the formation of MeOH and EtOH respectively, during the final oxidation step with ethylene glycol. Therefore, the only implication from an industrial view point would be the need to remove two waste solvents at the end of the process.

NaM was the least active zeolite; GC analysis of the reaction mixture established that no reaction had taken place and naphthalene was recovered quantitatively.

HM was found to be the most active zeolite, giving a 33 % yield of the direct ethoxymethylation product, although bis-(EMN) was not observed. HM suffered from poor selectivity, with a 2/1 ratio of 1.9 observed. This was significantly lower compared to the reaction of naphthalene and DMM over HM (where a 2/1 ratio of 13.0 was observed).

The main advantage of DEM over DMM as the alkoxyalkylating reagent was the improved recovery of material from the reaction mixture, since nearly all material was accounted for in every reaction. The di-substituted product was not generated during the ethoxymethylation of naphthalene; therefore it was unlikely that any tri or poly substituted compounds were generated, which in turn would mean coking of the zeolite leading to a low recovery of material from the reaction mixture would not occur, as observed.

3.1.7 Discussion

The results from the initial methoxy/ethoxymethylation of naphthalene over different zeolites (Tables 3.1.1 and 3.1.2 respectively) demonstrated the relative advantages and disadvantages of each zeolite with dimethoxymethane and diethoxymethane as the alkoxyalkylating reagents.

After consideration of these results it was decided that the methoxymethylation of naphthalene over Hβ would be investigated more extensively. Although Hβ suffered from poor selectivity and approximately 25 % of material was not recovered from the reaction mixture, it gave the highest yield of MMN (19 %), and in addition to this bis(MM)N (6 %) was also observed. This was of great significance in terms of

the aim of this part of the thesis (set out in Section 3.1), which was to generate bis-(MM)N in reasonable yield with the selectivity of the reaction favouring the 2,6-isomer.

Even though the yield of bis(MM)N was modest and at this stage and it was not clear which isomers of bis(MM)N were generated (3 isomers detected with Mr 216), the reaction showed potential and provided a solid platform on which to build.

The ethoxymethylation of naphthalene over HM gave a higher yield of EMN than the comparable yield of MMN from the methoxymethylation of naphthalene over Hβ (33 % EMN, 19 % MMN respectively), however, no bis(ethoxymethyl)naphthalenes were generated. Therefore, this reaction was not selected for optimisation at this stage.

In conclusion, the methoxymethylation of naphthalene catalysed by Hβ gave the most promising results from the initial series of experiments undertaken. Therefore, this reaction was investigated further.

3.1.8 Yield optimisation of (methoxymethyl)naphthalene formation

3.1.8.1 Investigating different reaction parameters

A series of optimisation reactions were carried out in which several reaction parameters were varied in an attempt to increase both the yield and selectivity of the desired product. These included reactions designed to probe the effects of reaction temperature, length of reaction, amount of catalyst, concentration of reagent and the type of solvent employed. The results are shown in the following sections. The first study involved varying the solvent to establish whether cyclohexane was the optimal solvent (in terms of activity and selectivity), several solvents were compared including hexane, acetone, chloroform, diethylether and cyclohexane, with dimethoxymethane as the alkoxyalkylating reagent and Hβ as the catalyst. The results are shown in Table 3.1.3.

3.1.8.2 Varying solvent with Hβ

Table 3.1.3: Effect of varying solvent in the reaction of dimethoxymethane with naphthalene over zeolite Hβ[a]

Solvent	Cyclohexane	Hexane	Acetone	Chloroform	Diethylether
Swansea experiment code	D14a	D14b	D14c	D14d	D14f
Naphthalene recovery (%)	45	53	48	46	63
Methylnaphthalenes (%)	3	3	1	2	6
MMN (%	19	13	22	21	4
2/1 ratio	1.9	1.8	2.5	2.6	3.5
bis(MM)N (%)	6	0	5	3	0
Total (%)	73	69	76	72	73

[a] 18 h stirred mini reactor reactions at 150 °C under self generated pressure; catalyst (4 g Hβ Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (6.03 g, 80 mmol) and solvent (60 ml).

The results observed with both acetone and chloroform were comparable to those with cyclohexane in terms of the yield of MMN (22 % and 21 % respectively compared to 19 % with cyclohexane), although the yield of bis(MM)N decreased slightly (5 % and 3 % yields were observed with acetone and chloroform respectively, compared to a 6 % yield with cyclohexane). An increase in selectivity was achieved with both acetone and chloroform (2/1 ratio of 2.5 and 2.6 respectively, compared to a 2/1 ratio of 1.9 for cyclohexane).

When hexane was employed as the solvent the reaction produced a lower yield, the yield of MMN decreasing to 13 % and bis(MM)N not being obtained. The reaction was also less selective with hexane when compared to cyclohexane (2/1 ratio 1.8 and 1.9 respectively).

The highest selectivity was achieved with diethyl ether (2/1 ratio of 3.5), but this was at the expense of the activity. Very little reaction occurred and MMN was observed in only a 4 % yield, with no formation of bis(MM)N.

These results suggest that there was no significant improvement to either the selectivity or the activity of the reaction by incorporating a different solvent. Therefore, cyclohexane continued to be the solvent of choice for further experimentation.

All previous reactions were carried out at 150 °C for 18 h (150 °C was chosen as a suitable mid way temperature and 18 h as a suitable reaction time in order for the reactions to be easily worked up and analysed in a single day). The best yield of MMN so far in cyclohexane was 19 %, with a 2/1 ratio of 2.9 and 6 % of bis(MM)N. The effect of reaction time and temperature were studied in an attempt to improve the yield and selectivity of this desired product.

3.1.8.3 Varying reaction temperature with Hβ

An initial study was conducted where the reaction temperature was varied between 100 °C and 200 °C and the results are presented in Table 3.1.4. The selectivity of the reaction was not greatly improved on varying the reaction temperature, although the reaction was somewhat more selective at 100 °C (2/1 ratio of 3.1 compared to 2/1 ratio of 1.9 at 150 °C). However, this was at the expense of the activity and the reaction occurred only a small extent Neither bis(MM)N nor methylnaphthalenes were generated at 100 °C and MMN was observed in a modest 5 % yield. An increase in product recovery from the reaction mixture was observed at 100 °C, with 90 % of material being recovered compared with only 73 % recovery of material at 150 °C.

When the temperature was increased to 125 °C the yield of product significantly increased compared to 100 °C. The reaction was comparable to the original reaction (Table 3.3) carried out at 150 °C, in terms of the yield of MMN (20 % at 125 °C compared to 19 % at 150 °C), although the yield of bis(MM)N was lower at 125 °C (2 % compared to 6 % at 150 °C). Methylnaphthalene was also generated in a lower yield at 125 °C compared to 150 °C (1 % yield and 3 % yield respectively). The recovery of material from the reaction mixture was similar (75 % at 125 °C compared with 73 % at 150 °C).

When the reaction temperature was increased above 150 °C the yield of MMN decreased considerably. MMN was generated only in a 6 % yield at 180 °C and it was not detected at all at 200 °C. In addition to this Bis(MM)N was not detected at either 180 °C or 200°C. Conversely, at 180 °C, methylnaphthalene was obtained in the same yield as it was at 150 °C (3 %) and actually increased to 8 % at 200 °C.

Even though the yield of desired products decreased on increasing the temperature above 150 °C, the extent of reaction actually increased, resulting in an increase in the conversion of naphthalene. The conversion was greatest at 200 °,C where the highest naphthalene conversion (72 %) was observed.

The decrease in yields of both MMN and bis(MM)N, coupled with an increase in naphthalene conversion, led to a decrease in product recovery from the reaction mixture at elevated temperatures. Only 53 % and 36 % recoveries of material were recorded at 180 °C and 200 °C respectively, and in both cases the product largely comprised of unreacted naphthalene. This was compared to a 73 % recovery of material from the reaction mixture at 150 °C, which comprised a mixture of Menap, MMN, bis(MM)N and unreacted naphthalene.

It was apparent from these results that there was no advantage from increasing the reaction temperature, in terms of increased product yield, enhanced selectivity or improved product recovery. It was also noted that the reaction at 125 °C was comparable to the reaction at 150 °C, with neither the yield of MMN nor the selectivity diminishing on decreasing the reaction temperature to 125 °C .

In light of this information it was decided to conduct a second temperature study where a smaller range of temperatures were investigated in order to establish the optimum temperature for the methoxymethylation of naphthalene. The temperature was varied in 5 °C stages from 115 °C to 135 °C. The results are given in Table 3.5.

It was found that on increasing the reaction temperature the selectivity of the reaction decreased slightly (2/1 ratio of 2.9 at 115 °C compared with a 2/1 ratio of 2.0 at 135 °C). Within experimental error the reaction at 120 °C (2/1 ratio of 3.0) was essentially identical to that at 115 °C (2.9)

With regard to the amount of quantities of products obtained, the yield of MMN was almost identical (between 18 % and 20 %) for each of the reactions between 115 °C and 135 °C, while a slight increase in bis(MM)N was observed when the temperature was increased (2 % yield was observed at 125 °C compared to 4 % yield at 135 °C). A similar increase this was also observed for methylnaphthalene, where the yield increased from 1 % at 115 °C to 3 % at 135 °C.

The reaction was more rapid as the temperature was increased from 115 °C to 135 °C, resulting in an increased conversion of naphthalene (36 % naphthalene conversion and 53 % naphthalene conversion at 115 °C and 135 °C respectively). As with the previous set of experiments (set out in Table 3.4) , however, the increased conversion was not reflected in the yields of products obtained. Consequently, the

recovery of material from the reaction mixture decreased on increasing the reaction temperature (86 % of material was recovered at 115 °C compared to 74 % at 135 °C).

In summary, when the reaction was carried out below 115 °C an increase in product recovery was observed, but the reaction occurred to only a small extent giving, a low yield of MMN with no production of bis(MM)N. All the reactions carried out between 115 °C and 150 °C were very similar, the yields of mono and bis(MM)N increasing but the product recovery decreasing compared to the reaction carried out at 100 °C. When the temperature was increased further than 150 °C, the reaction produced a lot of non-recoverable material, with the yield of products decreasing drastically along with the total recovery of material from the reaction mixture.

It was evident from these two sets of experiments that the optimum temperature for the reaction was around 120 °C, in terms of the yield and selectivity of the desired products as well as the product recovery from the reaction mixture. Therefore further experiments were conducted at 120 °C.

Table 3.1.4: Varying the reaction temperature in the reaction of naphthalene and dimethoxymethane over Hβ[a]

Temp (°C)	100	125	150	180	200
Swansea experiment code	D19	D20	D21	D22	D23
Naphthalene recovery (%)	85	53	45	44	28
Methylnaphthalenes (%)	0	1	3	3	8
MMN (%)	5	20	19	6	0
2/1 ratio	3.1	2.6	1.9	2.3	/
bis(MM)N (%)	0	2	6	0	0
Total (%)	90	75	73	53	36

[a] 18 h stirred mini reactor reactions at varying temperatures, under self generated pressure; catalyst (4 g of Hβ Si/Al 25), naphthalene (1.28 g, 10 mmol), dimethoxymethane (6.03 g, 80 mmol) and cyclohexane as solvent (60 ml).

Table 3.1.5: Varying the reaction temperature in the reaction of naphthalene and dimethoxymethane over Hβ[a].

Temp (°C)	115	120	125	130	135
Swansea experiment code	D29	D30	D20	D31	D32
Naphthalene recovery (%)	64	56	53	46	47
Methylnaphthalenes (%)	1	1	1	2	3
MMN (%)	19	20	20	18	20
2/1 ratio	2.9	3.0	2.6	2.1	2.0
Bis(MM)N (%)	2	2	2	3	4
Total (%)	86	79	75	69	74

[a] 18 h stirred mini reactor reactions at varying temperatures, under self generated pressure; catalyst (4 g of Hβ Si/Al 251.), naphthalene (1.28 g, 10 mmol), dimethoxymethane (6.03 g, 80 mmol) and cyclohexane as solvent (60 ml).

3.1.8.4 Varying reaction time with Hβ

A series of experiments was carried out where the reaction time was varied from 2 h to 72 h in an attempt to establish the optimum length of reaction, in terms of the best yield and selectivity of the desired product. The results are set out in Table 3.1.6.

Table 3.1.6: Varying the reaction time in the reaction of naphthalene and dimethoxymethane over Hβ[a].

Time (h)	2	4	6	9	18	36	72
Swansea experiment code	D36	D37	D38	D33	D30	D34	D35
Naphthalene recovery (%)	71	59	55	54	56	54	49
Methylnaphthalenes (%)	0	1	2	1	1	3	6
MMN (%)	10	18	16	20	20	21	21
2/1 ratio	2.6	2.6	3.0	2.5	3.0	2.5	2.2
Bis(MM)N (%)	0	1	2	2	2	2	2
Total (%)	81	79	75	77	79	80	78

[a] Stirred mini reactor reactions at 120 °C, under self generated pressure at varying reaction times, catalyst (4 g of Hβ Si/Al 25), naphthalene (1.28 g, 10 mmol), dimethoxymethane (6.03 g, 80 mmol) and cyclohexane as solvent (60 ml)

The selectivity of the reaction was largely unaffected on increasing the reaction time from 2 h to 72 h. A 2/1 ratio of 2.6 was observed when the reaction was carried out for 2 h compared to a 2/1 ratio of 2.2 when the reaction was carried out for 72 h. This shows that the relative amounts of the 2 and 1 isomers of MMN in the reaction mixture did not vary when the reaction was left for long periods of time, which gave an indication of the stability of the isomers under the reaction conditions.

It was found that an increase in the reaction time gave rise to an increase in the conversion of naphthalene. This effect was more pronounced when the reaction time was increased from 2 h (29 % conversion) to 4 h (41 % conversion). When the reaction time was increased further the increase in conversion was not as significant, only a further 10 % increase in conversion being observed when the length of reaction was increased from 4 h to 72 h. (41 % and 51 % conversion, respectively).

The same trend was observed regarding the formation of MMN where the % yield of MMN increased on increasing the length of reaction. Once again this was more apparent when the reaction time was increased from 2 h to 4 h (At 2 h a 10 % yield of MMN was observed compared to an 18 % yield of MMN at 4 h). When the reaction was left for 18 h the yield of MMN only increased by 2 % to give a 20 % yield of MMN, which only increased to 21 % when the reaction was left for 72 h.

The yield of the side product methylnaphthalene also increased slightly on increasing the length of reaction; it was generated in a 1 % yield after 4 h, which increased to a 6 % yield when the reaction was carried out for 72 h. Furthermore, in this case it appeared that the increase was more uniform with half of the 6 % appearing during the last 36 h of the reaction. The effect of increasing the reaction time had little effect on the formation of bis(MM)N. bis(MM)N was not generated when the reaction was carried out for 2 h and was only observed in a 2 % yield when the reaction time was increased to 6 h. The yield did not increase any further even when the reaction was left for 72 h.

The fact that the conversion and product formation both increased in the same magnitude meant that the recovery of material did not decrease on increasing the length of reaction (as seen with previous reactions under forcing conditions). The amount of material recovered from the reaction mixture at 2 h was comparable to the reaction carried out at 72 h (81 % and 78 % respectively).

These results suggest that at 2 h the reaction had not yet reached completion but by 4 h the majority of the reaction had occurred, given that there was hardly any further product formation when the reaction was left for longer. Therefore, there was no added benefit in carrying out the reaction for longer than 4 h in terms of product yield and selectivity. Furthermore, if the reactions were carried out at 4 h they could

still be worked up and analysed in a single day. In view of this the length the standard reaction time in subsequent reactions was reduced from 18 h to 4 h.

It was interesting to note that the reaction appeared to come to a halt after several hours, despite the fact that both naphthalene and dimethoxymethane, the two reactants, remained in the reaction mixture. One possible explanation for this could be that equilibrium had been established. Another could be that the zeolite catalyst had become deactivated. In the former case, use of an increased quantity of zeolite should speed up the process of establishing equilibrium, but should not significantly change the position of the equilibrium. However, in the case that zeolite deactivation was responsible for the reaction stopping. Then use of a larger quantity of zeolite might result in a higher yield of products prior to its deactivation. A series of reactions were therefore conducted in which the amount of catalyst was varied under the new conditions of 4 h and 120 °C, in an attempt to increase the yield of MMN. The results are presented in Table 3.1.7.

3.1.8.5 Varying the amount of catalyst

Table 3.1.7: Varying the amount of Hβ catalyst in the reaction of naphthalene and dimethoxymethane[a]

Amount of HBeta (g)	0.5	1	2	4	6	8
Swansea experiment code	D39	D40	D41	D38	D43	D44
Naphthalene recovery (%)	98	83	78	59	42	40
Methylnaphthalenes (%)	0	1	2	1	2	1
MMN (%)	0	6	9	18	18	14
2/1 ratio	_	3.2	2.8	2.6	2.3	2.7
Bis(MM)N (%)	0	0	0	1	1	0
Total (%)	98	90	89	79	65	55

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (varying amounts of Hβ Si/Al 25), naphthalene (1.28 g, 10 mmol), dimethoxymethane (6.03 g, 80 mmol) and cyclohexane as solvent (60 ml)

In general, the yield of MMN increased on increasing the amount of Hβ, although the relationship between product formation and the amount of catalyst employed was not directly proportional

When 0.5 g of Hβ was employed virtually no reaction took place and naphthalene was recovered quantitatively. On increasing the amount of catalyst to 1 g, the reaction occurred to a small extent generating 6 % of the mono methoxymethation product as well as 1 % of methylnaphthalene, but bis(MM)N was not produced. Use of 2 g of catalyst gave a slightly higher yield of methylnaphthalene (2 %) and MMN (9 %), but once again bis(MM)N was not generated. With 4 g of catalyst the yield of MMN significantly increased to 18 % and bis(MM)N was generated in a 1 % yield. No further product formation was observed when the amount of catalyst was

increased to 6 g and the yield of MMN levelled off (18 %). When the amount of catalyst was increased even further to 8 g, the yield of MMN actually decreased to 14 % and no bis(MM)N was observed.

The selectivity of the reaction was largely unaffected by the amount of Hβ added to the reaction and the 2/1 ratio ranged from 3.2 with 1 g of Hβ (most selective reaction) to 2.7 with 8 g of Hβ.

The most notable trend that emerged from the results was the increase in the conversion of naphthalene on increasing the amount of catalyst. A 22 % naphthalene conversion was observed when 2 g of Hβ was employed which increased to 41 % when 4 g of Hβ was employed. The naphthalene conversion increased even further (60 %) when 8 g of catalyst was employed.

The product formation did not increase to the same degree (also seen previously on increasing the reaction temperature in Table 3.1.4) and the yield of MMN actually decreased when 8 g of catalyst was employed. Consequently, the recovery of material from the reaction mixture steadily decreased on increasing the amount of catalyst to the reaction mixture (98 % of material was recovered when 0.5 g of Hβ was employed compared to 55 % of recovered material when 8 g was added).

In summary, if the amount of Hβ was less than 4 g the reaction was slower resulting in a lower yield of MMN. When more than 4 g of Hβ was employed, no further increase in MMN was observed and the recovery of material from the reaction mixture decreased. It was still not possible to decide upon which of the two explanations was the more likely, but one could conclude that the optimum amount of catalyst was 4 g, and therefore it was decided to continue to use 4 g of Hβ for further experiments.

At this stage a maximum 18 % yield of MMN was achieved even under forcing conditions. In an attempt to increase the yield of MMN even further it was decided to vary the concentration of the methoxymethylating agent (DMM).

3.1.8.6 Varying the concentration of dimethoxymethane

Several experiments were carried out to establish if increasing the concentration of DMM would result in an increase in the yield of MMN. The effect of the solvent on the activity and selectivity of the reaction was also determined. The total volume inside the reactor was kept constant (67 ml) and the relative proportions of solvent and reagent were varied (Table 3.1.8). The results are presented in Table 3.1.9.

It was found that by decreasing the amount of cyclohexane in the reaction mixture and increasing the amount of DMM the yield of both mono and bis(MM)N significantly increased without a decrease in the recovery of naphthalene-derived material from the reaction mixture.

When the amount of DMM was increased from 80 mmol to 160 mmol the yield of MMN increased slightly from 18 % to 20 % yield and there was no increase in the yield of bis(MM)N. A further increase in DMM (320 mmol) gave a more significant increase in MMN (34 %) and bis(MM)N (8 %). The yield increased even further to 38 % of MMN and 18 % of bis(MM)N when a neat reaction was carried out in the absence of solvent.

The selectivity of the reaction decreased slightly on increasing the amount of DMM. A 2/1 ratio of 2.6 was observed when the reaction mixture was more dilute (80 mmol DMM) compared to a 2/1 ratio of 1.4 when the reaction mixture was more concentrated (758 mmol).

In summary, a maximum 38 % yield of MMN and 18 % yield of bis(MM)N was observed when 758 mmol of DMM was reacted with 10 mmol of naphthalene with 4 g of Hβ for 4 h at 120 °C, in the absence of solvent. This suggests that there was no benefit in incorporating solvent into the reaction mixture (in terms of product yield or selectivity) therefore all further reactions were carried out with excess DMM (758 mmol) in the absence of solvent.

Table 3.1.8: Reagent and solvent ratios (expressed in grams and millilitres), corresponding to the change in concentration in the reaction between dimethoxymethane and naphthalene catalysed by Hβ (as described in **Section 3.1.8.6.)**

Swansea Experiment Code	D37	D45	D46	D47	D48
Dimethoxymethane (mmol)	80	160	320	640	758
Dimethoxymethane (g)	6.1	12.2	24.3	48.6	57.6
Dimethoxymethane (ml)	7	14	28	57	67
Cyclohexane (g)	46.8	41.3	30.4	7.8	0
Cyclohexane (ml)	60	53	39	10	0
Total (g)	52.9	53.5	54.7	56.4	57.6
Total (ml)	67	67	67	67	67

Table 3.1.9: Results to show the effect of varying the concentration of dimethoxymethane in the reaction of naphthalene and dimethoxymethane over Hβ zeolite[a]

Reagent (ml)	7	14	28	57	67
Solvent (ml)	60	53	39	10	0
Swansea experiment code	D37	D45	D46	D47	D48
Naphthalene recovery (%)	59	55	36	22	18
Methylnaphthalenes (%)	1	1	1	3	0
MMN (%)	18	20	34	40	38
2/1 ratio	2.6	3	3.1	2.5	1.4
Bis(MM)N (%)	1	1	8	15	18
Total (%)	79	77	79	80	74

[a] 4 h stirred mini reactor reactions at 120 °C, under self generated pressure; catalyst (4 g Hβ Si/Al 25), naphthalene (1.28 g, 10 mmol), dimethoxymethane and cyclohexane as solvent.

The previous set of experiments demonstrated that the yield of MMN significantly improved when the reaction was carried out in excess reagent and a 38 % yield of MMN along with an 18 % yield of bis(MM)N was observed. However, the reaction did not reach completion and unreacted naphthalene was recovered from the reaction mixture (18 % recovery). The reaction was carried out under relatively mild conditions (120 °C for 4 h) as it was found that forcing conditions (high temp and increased catalyst) brought about a decrease in both the yield of MMN and bis(MM)N as well as a decrease in the product recovery from the reaction mixture. In theory it was a possibility that the remaining naphthalene would react further under more forcing reaction conditions in the presence of excess reagent.

In view of this, it was decided to conduct a second optimisation study in an attempt to increase the yield of the desired products and push the reaction to completion. Several reactions were carried out in excess DMM and the reaction conditions were varied. These conditions included reaction time, temperature, volume of reagent and the amount of catalyst. The results are discussed in the following sections.

3.1.8.7 Varying the length of reaction with excess dimethoxymethane

The length of the reaction was varied from 1 h to 8 h and the results are presented in Table 3.1.10. The selectivity was not significantly affected on varying the length of reaction. When the reaction time was increased from 1 h to 8 h a slight decrease in selectivity was observed, with a 2/1 ratio of 2.6 being achieved when the reaction was carried out for 1 h compared to a 2/1 ratio of 2.1 when the reaction was carried out for 8 h.

It was found that the extent of the reaction increased on increasing the reaction time and an increase in naphthalene conversion was observed. A 36 % conversion was achieved when the reaction was carried out for 1 h, but this significantly increased to 82 % when the reaction time was increased to 4 h. When the reaction was carried out at 6 h and 8 h the reaction did not proceed any further and the conversion levelled off (80 % and 79 % naphthalene conversion observed at 6 h and 8 h, respectively).

The yields of MMN and bis(MM)N increased when the reaction time was increased from 1 h to 4 h, but a decrease in the yield of product formation was observed when the reaction time was increased further than 4 h. At 1 h a 21 % yield of MMN was achieved along with a 2 % yield of bis(MM)N, while on increasing the reaction time to 2 h the yields of both MMN and bis(MM)N increased to 30 % and 8 % respectively. The yield of products increased even further when the length of

reaction was increased to 4 h, with MMN being observed in a 38 % yield and bis(MM)N being observed in an 18 % yield. Conversely, the yields of product decreased when the length of reaction was increased beyond 4 h. A 20 % yield of MMN was observed with an 8 % yield of bis(MM)N when the reaction was carried out for 8 h.

The decrease in product formation observed when the reaction time was increased beyond 4 h was not comparable to the degree of naphthalene conversion observed. The conversion did not decrease when the reaction time exceeded 4 h; consequently, the recovery of material from the reaction mixture decreased. A total of 87 % of naphthalene-containing material was recovered from the reaction mixture when the reaction was carried out for 1 h, compared to a 49 % recovery of material from the reaction mixture when the length of reaction was increased to 8 h.

From the fact that the conversion of naphthalene levelled off at around 80 % after about 4 h, it appears that either equilibrium had been established or that the catalyst had been deactivated. However, it is clear that degradation of the products still continued, so that the yields of desirable products decreased when the reaction time exceeded 4 h.

Table 3.1.10: Results to show effect of time with excess dimethoxymethane in the reaction of naphthalene and dimethoxymethane over Hβ zeolite[a]

Time (h)	1	2	4	6	8
Swansea experiment code	D49	D50	D48	D51	D52
Naphthalene conversion (%)[b]	36	54	82	80	79
Naphthalene recovery (%)[b]	64	46	18	20	21
Methylnaphthalenes (%)[b]	0	0	0	0	0
MMN (%)[b]	21	30	38	31	20
2/1 ratio[c]	2.6	2.4	2.2	2.4	2.1
Bis(MM)N (%)[b,]	2	8	18	9	8
Total (%)[b]	87	84	74	60	49

[a] Stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ Si/Al 25), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

Given that the product yield decreased on prolonging the reaction time, it was useful to keep a relatively short time for the reaction. In view of this, all further reactions continued to be carried out for 4 h.

3.1.8.8 Varying the reaction temperature with excess dimethoxymethane

Table 3.1.11: Results to show the effect of temperature with excess reagent in the reaction of naphthalene and dimethoxymethane over Hβ zeolite[a]

Temp (°C)	80	100	120	140	160
Swansea experiment code	D53	D54	D48	D56	D56a
Naphthalene recovery (%)	97	83	18	17	13
Methylnaphthalenes (%)	0	0	0	0	<1
MMN (%)	3	13	38	30	23
2/1 ratio	3.5	2.7	2.0	2.1	1.5
Bis(MM)N (%)	0	0	18	21	20
Total (%)	100	96	74	68	57

[a] 4 h stirred mini reactor reactions at various temperatures under self generated pressure; catalyst (4 g Hβ Si/Al 25), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

A series of experiments was carried out where the reaction temperature was increased from 80 °C to 160 °C in 20 °C stages. The results are presented in Table 3.1.11. Increasing the reaction temperature from 80 °C to 160 °C resulted in a slight decrease in selectivity, a 2/1 ratio of 3.5 being observed when the reaction was carried out at 80 °C compared to a 2/1 ratio of 1.5 when the reaction was carried out at 160 °C.

A similar trend was observed to that seen in the previous temperature studies (reported in Tables 3.4 and 3.5) with regard to product formation on increasing the reaction temperature, where the yield of products increased as the reaction temperature was increased from 80 °C to 120 °C, but no further increase in product formation was observed when the temperature was increased past 120 °C.

The reaction occurred to a small extent at 80 °C (3 % conversion) and a 3 % yield of MMN was observed. In addition to this there was a 100 % recovery of

material from the reaction mixture. This was not surprising, as one would expect the side reactions (that contribute to the low recovery of material from the reaction mixture) to be less favoured at 80 °C due to the slow reaction observed.

The conversion increased when the reaction temperature was increased to 100 °C (17 % naphthalene conversion at 100 °C compared with 3 % conversion at 80 °C), leading to an increase in MMN formation, where a 13 % yield was observed. A high recovery of material was still observed at 100 °C even though the conversion was greater, and almost all of the material was recovered from the reaction mixture (96 %). However bis(MM)N was not observed when the reaction was carried out at either 80 °C or 100 °C.

The reaction proceeded to a significantly greater extent at 120 °C and the conversion dramatically improved (82 % naphthalene conversion observed at 120 °C compared with a 17 % conversion at 100 °C). The quantity of MMN observed also increased and a 38 % yield was achieved. In addition to this, bis(MM)N was observed in an 18 % yield, although, the product recovery from the reaction mixture decreased (74 % of material was recovered).

A further small increase in conversion was observed when the reaction temperature was increased to 140 °C (83 % conversion) and 160 °C (87 % conversion), but the yield of MMN decreased, with a 30 % yield being observed at 140 °C and a 23 % yield being observed at 160 °C.

Conversely the yield of bis(MM)N increased slightly to 21 % when the reaction temperature was increased to 140 °C, although no further increase was observed on increasing the reaction temperature to 160 °C (20 % yield observed).

As seen with the previously conducted temperature studies, a steady decline in the recovery of material from the reaction mixture was observed on increasing the reaction temperature from 120 °C to 160 °C. This resulted from an increase in the conversion coupled with a decrease in the quantity of products observed (57 % of material was recovered at 160 °C compared to a 68 % recovery at 140 °C). It was thought that coke formation was exacerbated at elevated temperature.

In conclusion, neither the yield of MMN or bis(MM)N improved when the reaction temperature was increased above 120 °C. Therefore, further experiments would still be conducted at 120 °C.

3.1.8.9 Varying the volume of reagent with Hβ

The previous set of experiments were carried out in an excess of DMM (758 mmol: the maximum volume that the reaction vessel could contain) free from any solvent, as this gave the best yields of both MMN and bis(MM)N when variations of solvent-DMM mixtures had been tested. In that series, the concentrations of DMM in cyclohexane had varied across the series as well as the quantity of DMM used. It was of interest to know whether a different (smaller) volume of neat DMM might have advantages, since this would increase the concentration of naphthalene in the mixture.

A series of reactions was therefore carried out to determine the effect of the volume of DMM on the product yield. The volume of DMM was varied from 80 mmol to 758 mmol (in the absence of cyclohexane), for reactions carried out for 4 h at 120 °C. The results are presented in Table 3.1.12.

It was found that varying the volume of reagent did not change the selectivity of the reaction. A 2/1 ratio of 2.1 was observed when the reaction was carried out in 80 mmol of DMM compared to a 2/1 ratio of 2.2 when the reaction was carried out in 758 mmol of DMM.

The conversion actually decreased on decreasing the volume of DMM, to give a decrease in both conversion and the yield of products. When 80 mmol of DMM was employed a 52 % conversion was observed, while MMN was achieved in a 20 % yield along with a 2 % yield of bis(MM)N. When the quantity of DMM was 160 mmol the conversion increased slightly to 60 % and there were increases in the yields of both MMN and bis(MM)N (26 % yield and 8 % yield respectively).

This trend was also observed when the quantity of reagent was increased to 320 mmol (32 % MMN and 12 % bis(MM)N obtained) and 640 mmol (35 % MMN and 15 % bis(MM)N obtained). When the maximum volume of DMM was employed (758 mmol) the conversion increased even further to 82 % and a 38 % yield of MMN and an 18 % yield of bis(MM)N were obtained.

The recovery of material was largely unaffected by the volume of reagent. There was a fluctuation within just a 10 % range when the volume of DMM was raised from 80 mmol to 758 mmol. A 70 % recovery of material was achieved when the reaction was carried out in the presence of 80 mmol of DMM compared to a 74 % recovery of material when the reaction was carried out in the presence of 758 mmol of DMM, with the maximum recovery recorded at 83 % with 640 mmol of DMM.

One can conclude that the greater the volume of DMM employed in the reaction the greater the conversion was. It appeared that a large excess of DMM encouraged the reaction to go further to give a higher yield of both MMN and bis(MM)N. Therefore reactions continued to be carried out with 758 mmol (67 ml) of DMM.

Table 3.1.12: Varying the volume of dimethoxymethane in the reaction of naphthalene and dimethoxymethane over Hβ zeolite[a]

Reagent (mmol)	80	160	320	640	758
Swansea experiment code	D57	D58	D59	D60	D48
Naphthalene recovery (%)	48	40	34	33	18
Methylnaphthalenes (%)	0	0	0	1	0
MMN (%)	20	26	32	35	38
2/1 ratio	2.1	2.1	2.1	2.1	2.2
Bis(MM)N (%)	2	8	12	15	18
Total (%)	70	74	78	83	74

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (varying amounts).

3.1.8.10 Varying the amount of catalyst with excess reagent

Even in the presence of a large excess of reagent, at elevated temps and increased reaction times the reaction did not reach completion and unreacted naphthalene was recovered from the reaction mixture. Therefore, experiments were carried out where the amount of catalyst was increased, in an attempt to push the reaction further and increase product formation. Reactions were carried out where the amount of Hβ was varied from 0.5 g to 8 g and the results are presented in Table 3.1.13.

A minor decrease in the 2/1 ratio was observed when the amount of catalyst employed in the reaction was increased from 0.5 g to 8 g. A 2/1 ratio of 1.8 was observed when the reaction was carried out in the presence of 0.5 g of catalyst compared to a 2/1 ratio of 1.1 when the reaction was carried out in the presence of 8 g of catalyst. However, the ratio was higher than with 4 g of zeolite and the decrease observed with the greater quantity was accompanied by conversion of some of the MMN into bis(MM)N, which would have affected the ratio.

The conversion increased significantly when the amount of catalyst employed in the reaction was increased from 0.5 g to 8 g. An 18 % conversion was observed in the presence of 0.5 g of Hβ and a 15 % yield of MMN was obtained. When the amount of catalyst was increased to 1 g the conversion increased to 23 % and the yield of MMN increased slightly to 16 %. A further increase in conversion (36 %) and yield of MMN (28 %) was observed when the amount of catalyst was increased to 2 g, but no di substituted product was obtained in these reactions.

Furthermore, when the reaction was carried out in the presence of 0.5 g to 2 g of Hβ, the conversion was consistent with the degree of product formation. Therefore,

a good recovery of material from the reaction mixture was observed (exceeding 90 %).

A big increase in conversion was observed when the amount of catalyst was increased from 2 g of Hβ to 4 g of Hβ (36 % conversion and 82 % conversion respectively). The yield of MMN also increased to 38 % and bis(MM)N was observed in an 18 % yield, yet the recovery of material decreased to 74 % when 4 g of Hβ was employed. This was in keeping with the theory of the presence of the side reactions of bis(MM)N, either with itself or naphthalene or MMN, to give large molecules that were not retractable from the zeolite leading to a low recovery of material.

The reaction almost reached completion on increasing the amount of catalyst to 8 g and a 92 % conversion was observed. However, a decrease in the yield of MMN was observed (29 % yield when 8 g of Hβ was observed compared to a 38 % yield when 4 g of Hβ was observed). Conversely the yield of bis(MM)N increased to 31 %, which was the highest yield of bis(MM)N observed so far. The increased yield in bis(MM)N was evidence that the reaction had gone further, so it would not be surprising that the yield of the mono compound would decrease, because it went on to react further to give the di substituted product. The recovery of material from the reaction mixture did not decline to a great extent and only a 5% decrease in the material recovery was observed when compared to the reaction where 4 g of Hβ was employed.

It was clear that the extent of the reaction increased on increasing the amount of Hβ and almost 100 % conversion of naphthalene was achieved when 8 g of Hβ was employed. The next goal was therefore a way of pushing the reaction to completion without the concomitant reduction in product recovery.

Table 3.1.13: Varying the amount of Hβ catalyst in the reaction of naphthalene and excess dimethoxymethane[a]

Amount of catalyst (g)	0.5	1	2	4	6	8
Naphthalene recovery (%)	82	77	64	18	20	8
Methylnaphthalenes (%)	0	0	0	0	0	1
MMN (%)	15	16	28	38	40	29
2/1 ratio	1.8	1.8	1.5	2.2	1.7	1.1
Bis(MM)N (%)	0	0	0	18	16	31
Total (%)	97	93	92	74	76	69

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (varying amounts of Hβ Si/Al 25), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

3.1.9 General Discussion

Points that seem to have emerged:

1. In order to achieve a worthwhile conversion, certain minimum conditions of temperature, amount of dimethoxymethane and Hβ, and time need to be employed.
2. After a certain time, even when the minimum conditions are employed, conversion of naphthalene almost stops, suggesting either equilibrium has been reached or the catalyst has been deactivated.
3. However, other reactions are able to continue in these conditions leading to reductions in MMN, bis(MM)N and production of material that cannot be extracted from the zeolite. These reactions apparently do not need active zeolite in order to proceed.
4. Need further information about why the conversion of naphthalene stops which is discussed at length in Section 2.

3.1.10 Summary and conclusions

From the initial methoxymethylation reactions, HY was the most active catalyst and resulted in the highest conversion being observed. However, the major product was methylenebis(naphthalene), an undesirable side product incorporating two molecules of naphthalene bridged by a methyl group. Hβ was found to be the most active catalyst in terms of the yield of the desired products (mono-MMN and bis(MM)N). HM was found to be the most selective catalyst but suffered from poor activity.

In contrast, HM was the most active catalyst for the ethoxymethylation of naphthalene, but this was at the expense of the selectivity. HZSM-5 was the most selective catalyst in the ethoxymethylation reactions. In general the ethoxymethylation of naphthalene (over various zeolites) was less selective when compared to the selectivity achieved during the methoxymethylation of naphthalene over HM.

In the initial survey, the methoxymethylation of naphthalene over Hβ gave the most encouraging results with a reasonable yield of MMN being observed and bis(MM)N also being generated. Therefore, this reaction was chosen for further optimisation. Reactions were carried out under forcing conditions (increase time and temp) and with more catalyst or more methoxymethylating agent added, in an attempt to increase the conversion of the reaction into the desired products coupled with an improvement in the recovery of material from the reaction mixture. The general trends are reported below.

Increasing reaction temp:

Increasing the reaction temperature resulted in increased conversion and increased MMN and bis(MM)N yields up to a point (120 °C and 150 °C respectively), and then a decrease, along with decreased selectivity and decreased recovery of material from the reaction mixture.

Increasing reaction time:

Increasing the reaction time resulted in increased conversion, increased MMN and bis(MM)N yields, increased 2/1 ratio, with little effect on amount of material recovered from the reaction mixture.

Increasing the amount of catalyst:

Increasing the amount of catalyst resulted in increased conversion, increased MMN yields up until 6 g then a decrease was observed, in these parameters, while the yield of bis(MM)N, the 2/1 ratio and the amount of material recovered from the reaction mixture all decreased.

Increasing the amount of methoxymethylating agent:

Increasing the amount of dimethoxymethane resulted in increased conversion, increased MMN and bis(MM)N yields, decreased 2/1 ratio, and little effect on the amount of material recovered from the reaction mixture.

It was found that when the reaction was carried out in excess reagent the yield of the desired products increased significantly. In an attempt to increase the conversion and yield of the desired product, a second optimisation study was carried and reactions were carried out in excess DMM under forcing conditions. The general trends are reported below.

Increasing reaction time:

Again, on increasing the reaction time the yields, conversion and selectivity tended to increase until 4 h. After longer reaction times the quantity of material recovered from the reaction mixture decreased.

Increasing reaction temp:

Increasing the reaction temperature in this set of reactions had the same results as in the previous series. Temperatures up to 120 °C were most useful.

Increasing the volume of methoxymethylating agent:

Increasing the volume of dimethoxymethane resulted in increased conversion, increased MMN and bis(MM)N yields, and decreased selectivity. The amount of material recovered from the reaction was largely unaffected.

Increasing the amount of catalyst:

Increasing the amount of catalyst resulted in increased conversion, increase in MMN yield up until 6 g and then a decrease. There was also a decrease in the amount of material recovered from the reaction mixture as the amount of zeolite used increased.

In conclusion, it was found that the reaction was limited under forcing reaction conditions and the yield of products and the recovery of material both decreased when too much force was used. This was thought to be due to secondary reactions which produced compounds that lead to the coking of the zeolite.

The best result so far was a 38 % MMN yield with a 2/1 ratio of 2.2 and an 18 % yield of bis(MM)N (3 isomers detected). This was achieved with naphthalene (10 mmol), DMM (758 mmol), Hβ (4 g) under relatively mild reaction conditions (4 h at 120 ° C). Although the best yield of bis(MM)N was 35 % when 8 g of Hβ was employed under the same conditions as those set out above, decreases in the yield and selectivity for MMN were also observed (29 % yield and 2/1 ratio of 1.1).

3.1.11 Experimental

3.1.11.1 General experimental

All instrumentation, analytical methods and reagents employed are included as an appendix.

3.1.11.2 Typical experimental procedure

Synthesis of (methoxymethyl)naphthalene from naphthalene and dimethoxymethane

All reactions were carried out in a mini reactor constructed and provided by Davey Process Technology. Heating and stirring of reaction mixture were achieved by means of a magnetic stirrer hot-plate, an oil bath and a internal magnetic follower. The temperature of the oil bath was controlled by a contact thermometer.

A magnetic stirrer bar was placed inside the bomb which was then charged with dimethoxymethane (6.08 g, 80 mmol), naphthalene (1.28 g, 10 mmol), cyclohexane (60 ml) and freshly calcined zeolite (4 g). The bomb was then sealed and placed in an oil bath. The reaction mixture was stirred at 150 °C for 18 h under self generated pressure (with 60 ml of cyclohexane the pressure was typically 50-100 psi for the duration of the reaction).

After the given reaction time the heat source was removed and the apparatus was cooled in an ice bath for 30 min.

The bomb was undone and its contents were transferred to a beaker. Any remaining zeolite residues were washed into the beaker with acetone. The zeolite was filtered using a sinter funnel at the pump and then extracted with acetone (100 ml) under reflux for 1 h.

The washings were combined and concentrated at the pump.

3.1.11.3 *Synthesis of (ethoxymethyl)naphthalene from naphthalene and diethoxymethane*

The same experimental procedure was followed for the ethoxymethylation of naphthalene (section 3.5.2) but diethoxymethane (8.32 g, 80 mmol) was substituted for dimethoxymethane.

3.1.11.4 *Synthesis of 2-(methoxymethyl)naphthalene from 2-naphthalenemethanol and iodomethane.*

tert-Butyllithium (7.0 ml, 12 mmol) was introduced to a stirred solution of 2-naphthalenemethanol (2.0 g, 12 mmol) in dry THF (40 ml) in a 200 ml round bottomed flask contained in an ice bath. The reaction mixture was stirred at 0 °C for 1 h under argon, MeI (10 ml, 160 mmol) was then introduced. The reaction mixture was stirred for a further 4 h at 40 °C under argon. The product mixture was treated with saturated ammonium chloride solution (20 ml). The organic layer was separated and the aqueous layer was extracted with diethylether (3 x 20 ml). The organic fractions were combined, washed with water (3 x 20 ml) and dried over magnesium sulfate. Solvents were removed at the pump to yield a yellow oil (2.04 g). The oil comprised a single component by GC analysis, and it corresponded to 2-(methoxymethyl)naphthalene (99 %).

1-(Methoxymethyl)naphthalene (89 %) and 1-(ethoxymethyl)naphthalene (75%) were prepared from 1-naphthalenemethanol and methyl or ethyl iodide, respectively, using the same procedure described above (as they are not known compounds).

3.1.12 GC analysis

Product mixtures were analysed by gas chromatography. A 1 μl sample was injected using a splitless technique.

The injector and detector temperature were set at 300 °C. Tetradecane was used as the internal standard. Helium was used as the carrier gas at a pressure of 9 psi.. The GC conditions used for the analysis are shown in **Figure 3.1.6.**

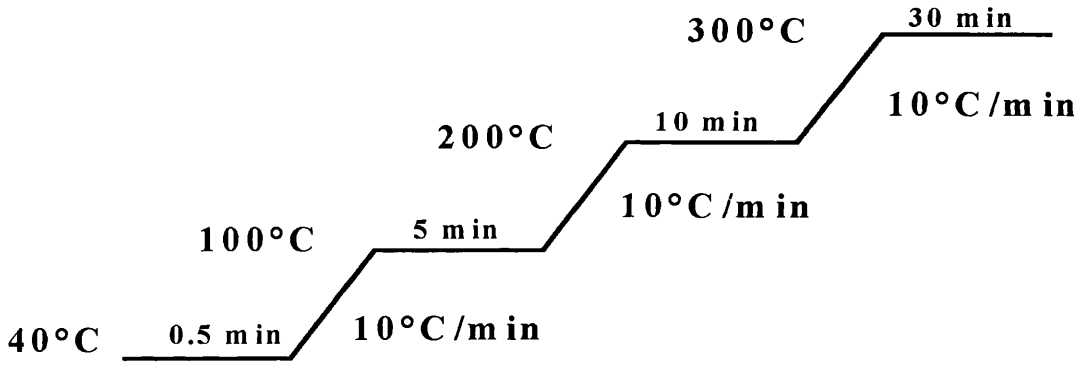


Figure 3.1.6: The GC conditions used for analysis of naphthalene product mixtures.

The GC traces of the product mixtures under these conditions gave the following results. Naphthalene had a retention time (Rt) of 25.3 min, tetradecane Rt 30.5 min. Analysis of reactions of dimethoxymethane and naphthalene gave peaks with retention times of 28.3 min and 29.9 min corresponding to 2- and 1-methylnaphthalenes, respectively. Peaks with retention times of 35.86 min and 36.14 min corresponded to 1-(methoxymethyl)naphthalene and 2-(methoxymethyl)naphthalene, respectively.

Several peaks were also observed with retention times 39.4, 44.1 and 44.3 min. GCMS analysis detected 3 compounds with Mr 216. This suggested the formation of three different isomers of bis(methoxymethyl)naphthalene. Separation of the isomers by fractional distillation was attempted several times with no success (due

to their similar physical properties). Consequently, the compounds were unable to be characterised further by NMR spectroscopy (characterisation of bis(MM)N will be discussed in Part 3 of this Chapter).

Peaks with retention times of 59.0 min, 59.4 min were also observed, GCMS analysis gave two compounds with Mr 268 corresponding to two isomers of methylenebis(naphthalene), a side product generated during the initial set of reactions of naphthalene and dimethoxymethane with HY.

The same difficulties (similar physical properties) were encountered with the separation of these isomers, which was also attempted several times by distillation and column chromatography to no avail. Therefore, pure samples of each isomer were not characterised

A mixture of the two isomers was analysed by both proton and carbon NMR, which showed that each of the two compounds contained two naphthalene rings, and one CH_2 group, suggesting the formation of two different isomers of MBN. GCMS gave signals corresponding to two compounds of Mr 268, which was also consistent with MBN.

One can speculate that the formation of the different isomers was dictated by the positions on the naphthalene rings that were bridged by the methyl group (i.e. the methyl group could bridge the two naphthalene rings at both the α positions to give 1,1-MBN, both β positions to give 2,2-MBN or between the α position on one naphthalene ring and the β position on the second naphthalene ring to give 1,2-MBN).

In the case of reactions between naphthalene and diethoxymethane, 1-(ethoxymethyl)naphthalene had a retention time of 37.7 min and 2-(ethoxymethyl)naphthalene had a retention time of 38.2 min. Peaks corresponding

to either monoethylnaphthalene or bis(ethoxymethyl)naphthalene were not detected by GC analysis.

3.1.12.1 Quantification of products - calculating response factors

Response Factors for reagents and products generated during the reactions were calculated using pure samples. The relative amounts of all products formed in each reaction were then quantified. Crude products were made up in a solution of known volume along with a known amount of internal standard and injected into the GC for analysis (conditions for analysis are outlined in **Section 3.1.14**). The yield of each product formed was calculated using the equations outlined in **Figure 3.1.7.**

$$\text{Rf of compound} = \frac{\text{Weight of Internal Standard}}{\text{Weight of Compound}} \times \frac{\text{Area of Compound}}{\text{Area of Standard}}$$

$$\text{Weight of compound} = \frac{\text{Weight of Internal Standard}}{\text{Rf of compound}} \times \frac{\text{Area of Compound}}{\text{Area of Standard}}$$

Figure 3.1.7: Equations used to quantify products formed

Pure samples of naphthalene, 1-methylnaphthalene and 2-methylnaphthalene were supplied by Aldrich. 1-(Methoxymethyl)naphthalene, 2-(methoxymethyl)naphthalene and 1-(ethoxymethyl)naphthalene were prepared by an authentic route (described in Section 3.5.4), from 1-naphthalenemethanol and 2-naphthalenemethanol, respectively, which were supplied by Aldrich.

A pure sample of 2-(ethoxymethyl)naphthalene was kindly supplied by Davey Process Technology.

Bis(methoxymethyl)naphthalene (mixture of 3 isomers) was separated from the crude reaction mixture by kugelrorh distillation under reduced pressure.

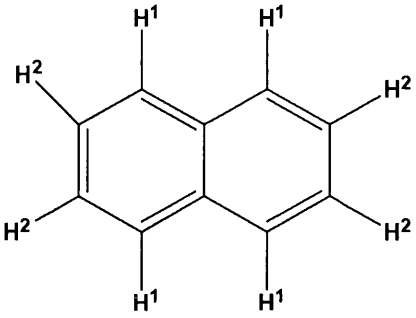
Methylenebis(naphthalene) (mixture of three isomers) was isolated from the crude mixture by column chromatography (hexane:diethyl ether, 90:10).

The spectral characterisation of relevant compounds described in this study are listed below.

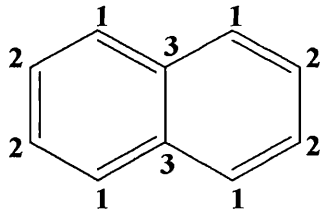
3.1.13 Analytical data

Naphthalene

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



$\delta^{1}H$: 7.75 (4H, dd, J = 6 and 3.3 Hz, H^1), 7.42 (4H, dd, J = 6 and 3.3 Hz, H^2).

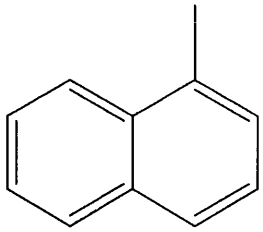


$\delta^{13}C$: 133.8 (C^3), 128.6 (C^1), 126.5 (C^2)

MS: From GCMS

EI m/z (% abundance): 128 (100) [M^+], 127 (80), 126 (35), 102 (63), 74 (49), 64 (61).

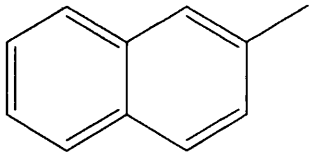
1-Methylnaphthalene



MS: From GCMS

EI m/z (% abundance): 142 (100) [M^+], 141 (89), 139 (15), 115 (23), 89 (3), 71 (5).

2-Methylnaphthalene

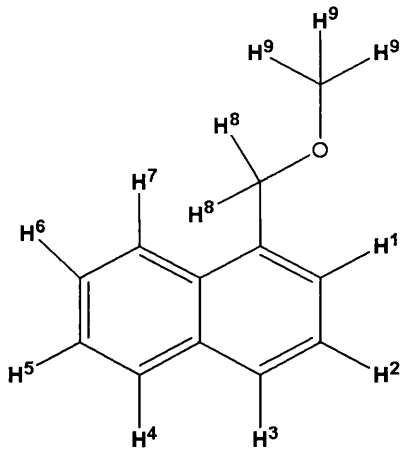


MS: From GCMS

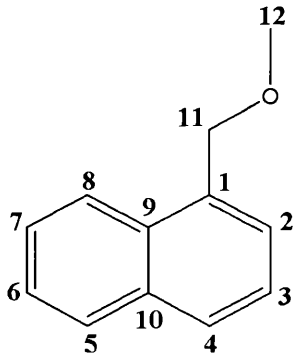
EI m/z (% abundance): 142 (100) [M^+], 141 (85), 139 (12), 115 (39), 89 (3), 71 (4).

1-(Methoxymethyl)naphthalene

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



$\delta^{1}H$: 8.00 (1H, Br d, J= 8 Hz, H^7), 7.75 (1H, Br d, J= 8 Hz, H^4), 7.68 (1H, Br d, J= 8 Hz, H^3), 7.39-7.45 (2H, m, H^6 and H^5), 7.37 (1H, Br d, J= 6 Hz, H^2), 7.32 (1H, Br d, J= 8 Hz, H^1) 3.45 (3H, s, H^9), 4.81 (2H, s, H^8).



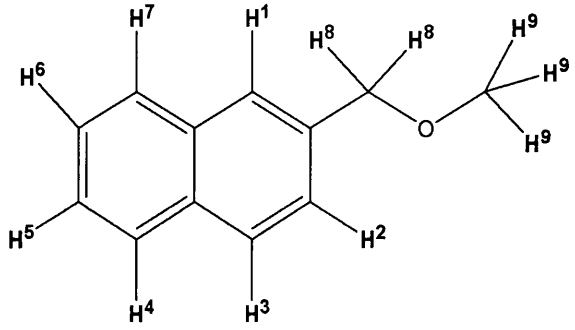
$\delta^{13}C$: 134.2 (C^{10}), 134.1 (C^9), 132.2 (C^1), 129.0 (C^5), 128.9 (C^4), 126.9 (C^7), 126.6 (C^6), 126.3 (C^3), 125.8 (C^2), 124.1 (C^8), 73.6 (C^{11}), 58.6 (C^{12}).

MS:

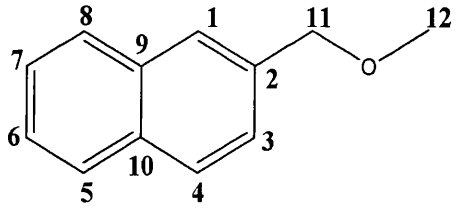
EI m/z (% abundance): 172 (75) [M^+], 171 (41), 155 (10), 142 (43), 141 (100), 128 (50).

2-(Methoxymethyl)naphthalene

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



$\delta^{1}H$: 7.67-7.72 (3H, broad signals, H^3, H^4 and H^7), 7.64 (1H, s, H^1), 7.30-7.37 (3H, m, H^2, H^5 and H^6), 4.53 (2H, s, H^8), 3.35 (3H, s, H^9)



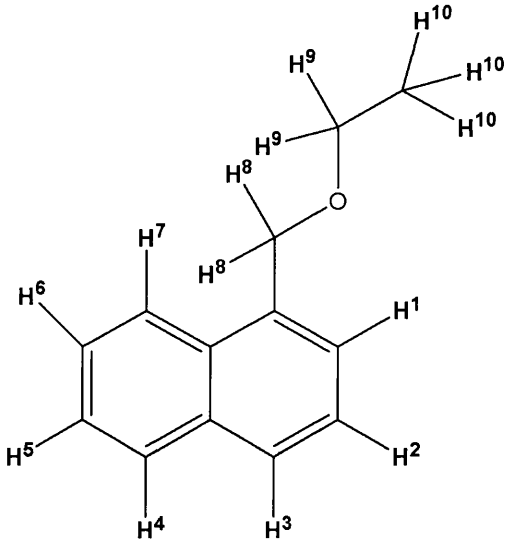
$\delta^{13}C$: 136.7 (C^2), 133.8 (C^9), 133.5 (C^{10}), 129.5 (C^3), 128.5 (C^5), 128.3 (C^8), 127.5 (C^4), 126.6 (C^1), 126.4 (C^6), 125.6 (C^7), 75.2 (C^{11}), 58.6 (C^{12}).

MS:

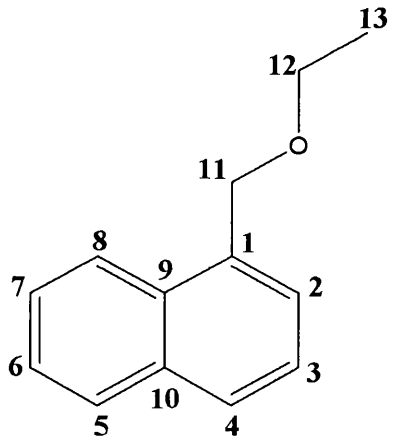
EI m/z (% abundance): 172 (80) [M^+], 155 (25), 142 (61), 141 (100), 128 (62), 115 (78).

1-(Ethoxymethyl)naphthalene

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



$\delta^{1}H$: 7.97 (1H, Br d, J= 8 Hz, H^7), 7.73 (1H, Br d, J= 8 Hz, H^4), 7.66 (1H, Br d, J= 8 Hz, H^3), 7.36-7.43 (2H, m, H^6 and H^5), 7.35 (1H, Br d, J= 7 Hz, H^2), 7.29 (1H, Br d, J= 8 Hz, H^1), 4.91 (2H, s, H^8), 3.61 (2H, q, J= 7 Hz, H^9), 1.15 (3H, t, J= 7 Hz H^{10}).

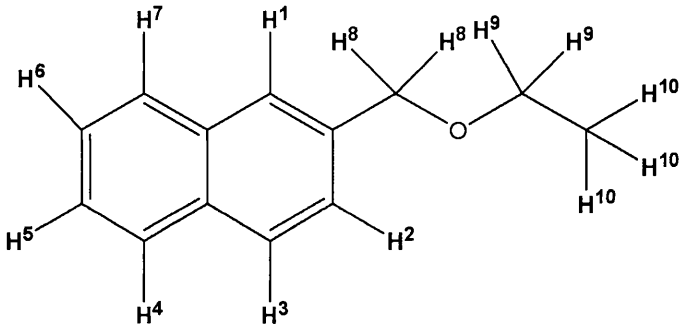


$\delta^{13}C$: 134.4 (C^{10}), 134.2 (C^9), 132.2 (C^1), 129.6 (C^5), 128.7 (C^4), 126.5 (C^7), 126.3 (C^6), 126.5 (C^3), 125.8 (C^2), 123.9 (C^8), 71.6 (C^{11}), 66.3 (C^{12}), 15.7 (C^{13}).

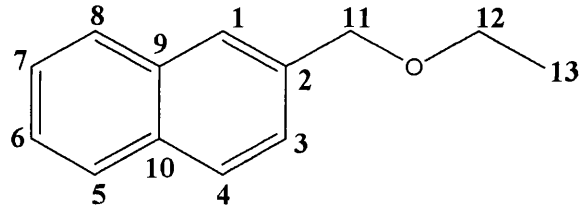
MS: EI m/z (% abundance): 186 (29) [M^+], 142 (87), 141 (100), 129 (62), 128 (37), 115 (52).

2-(Ethoxymethyl)naphthalene

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



$\delta^{1}H$: 7.71-7.77 (3H, broad signals, H^3, H^4 and H^7), 7.70 (1H, s, H^1), 7.37-7.42 (3H, m, H^2, H^5 and H^6), 4.61 (2H, s, H^8), 3.52 (2H, q, J= 7 Hz H^9), 1.15 (3H, t, J= 7 Hz H^{10}).

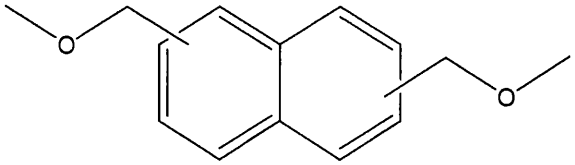


$\delta^{13}C$: 136.5 (C^2), 133.7(C^9), 133.4 (C^{10}), 128.6 (C^3), 128.3 (C^5), 128.1 (C^8), 126.7 (C^4), 126.5 (C^1), 126.2 (C^6), 126.1 (C^7), 73.2 (C^{11}), 66.2 (C^{12}), 15.7 (C^{13}).

MS:

EI m/z (% abundance): 187 (13), 186 (61) [M^+], 155 (31), 142 (42), 141 (100), 128 (62).

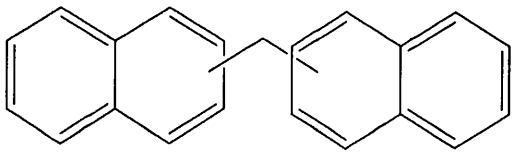
Bis(methoxymethyl)naphthalene mixture



MS: from GCMS

EI m/z (% abundance): 216 (93) [M^+], 185 (89), 171 (75), 141 (100), 115 (61).

Methylenebis(naphthalene) mixture



MS: From GCMS

EI m/z (% abundance): 268 (100) [M^+], 252 (54), 239 (7), 141 (33), 115 (52).

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Chapter 3, Part 2

Methoxymethylation of Naphthalene: Further Optimisation

3.2.1 Introduction

It was shown in Part 1 that the yields of MMN and bis(MM)N increased when dimethoxymethane was reacted with naphthalene under optimised conditions (4 h, 120 °C, 10 mmol naphthalene, excess DMM and 4 g of Hβ). However, the conversion of naphthalene stopped after 4 h and the yields of MMN and bis(MM)N levelled off, suggesting either equilibrium had been reached or the catalyst had been deactivated. Therefore, the aim of this section of work, was to establish why naphthalene conversion stopped, in the hope this could be overcome to increase the yields of MMN and bis(MM)N in the reaction under optimised conditions.

3.2.2 Establishing why product yields levelled off after 4 h

3.2.2.1 Deactivation of Hβ

The deactivation of zeolites, as a result of organic material (coke) blocking the pore channels and active sites of the zeolite, has been well documented in the literature[1-9]. It was shown in Section **3.1.5.3** in Part 1 of this Chapter that Hβ incorporated organic material during the course of the reaction; thus, it was reasonable to propose that naphthalene conversion stopped, because Hβ was deactivated.

3.2.2.2 Determining the activity of spent Hβ after a 4 h reaction under optimized conditions.

Experiments were conducted under optimised conditions, with spent Hβ (filtered from a reaction mixture after 4 h, from an optimised reaction). The extent of reaction that took place with spent Hβ was compared to the extent of reaction that took place with freshly calcined Hβ (under optimised conditions), to determine if the catalytic activity of Hβ was reduced during the course of the reaction.

3.2.2.3 Treatment of spent Hβ prior to reaction

An optimized reaction (**Reaction 1**) was carried out using the procedure outlined in Section **3.1.11** in Part1 of this Chapter, and spent Hβ was filtered from the reaction mixture at the pump, air dried overnight and weighed (4.50 g).

As discussed in Section **3.1.5.3** in Part 1 of this chapter, Hβ incorporated additional material, formed during the course of the reaction, that was not retractable. Therefore, the spent Hβ (after 4 h reaction) weighed more than the freshly calcined Hβ employed at the start of the reaction (4.0 g of Hβ employed at the start of the reaction compared to 4.50 g of spent Hβ obtained after the reaction).

The spent zeolite was split into two samples of equal weight. The first sample (**Sample A,** 2.25 g), was stored in a desiccator for 24 h over P_2O_5, to remove any moisture or volatile compounds. **Sample A** was reweighed, and the weight had decreased to 2.19 g, which was attributed to loss of water and evaporation of volatile compounds (e.g. DMM and acetone), adsorbed onto the zeolite during the reaction or work up procedure.

The second sample (**Sample B,** 2.25 g), was recalcined at 550 °C for 24 h, to burn off material incorporated into the zeolite framework during the reaction. **Sample B** was reweighed, and the weight had decreased to 2.00 g, suggesting material contained within the zeolite had been burnt off.

3.2.2.4 Reaction with spent Hβ under optimised conditions

Initially a reaction was carried out with **Sample A** (2.19 g) under optimized conditions and compared to the reaction with freshly calcined Hβ (2.0 g) using the procedure outlined in Section **3.1.11**, of Part1 of this Chapter. The results are reported in Table 3.2.1.

Table 3.2.1: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Determining the catalytic activity of the spent Hβ under optimized conditions[a]

	2 g, freshly calcined HBeta	2 g, Spent HBeta (Sample A)	2 g, Spent, Recalcined Hbeta (Sample B)
Swansea experiment code	OR2g	OR2gAD	OR2gcal
Naphthalene recovery (%)	64	82	64
Methylnaphthalenes (%)	0	0	0
MMN (%)	28	14	30
2/1 ratio	1.5	1.4	1.6
Bis(MM)N (%)	0	0	0
Total (%)	92	96	94

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (2 g Hβ, Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

The extent of reaction that took place with air dried spent Hβ, was appreciably less than the reaction with freshly calcined Hβ. An 18 % conversion of naphthalene was observed with **Sample A**, compared to a 36 % conversion of naphthalene with freshly calcined Hβ. The yield of MMN also decreased with **Sample A**, a 14 % yield being obtained, compared to a 28 % yield of MMN with freshly calcined Hβ (please note that bis(MM)N was not observed in either reaction).

These results illustrate that the catalytic activity of **Sample A** was lower than the catalytic activity of freshly calcined Hβ, suggesting that Hβ had been deactivated to some extent during the course of the **Reaction 1** (4 h, optimized reaction).

An identical reaction was carried out with **Sample B** (2.19 g). This reaction was compared to the reaction with freshly calcined Hβ (2 g), under the same conditions, to determine if the catalytic activity of Hβ was restored after recalcination. The results are reported in Table 3.21.

The reaction with spent, recalcined Hβ, was comparable to the reaction with freshly calcined Hβ and a 36 % conversion of naphthalene was observed in each reaction. The yield of MMN obtained in each reaction was almost identical also, and a 30 % yield of MMN was observed with spent, recalcined Hβ, and a 28 % yield of MMN was observed with freshly calcined Hβ.

These results illustrate how the activity of spent Hβ was restored after recalcination, which is an obvious advantage from an industrial viewpoint, with regards to the reusability of the catalyst[7].

In conclusion, it appeared that Hβ was deactivated to some extent during the course of **Reaction 1,** therefore offering a feasible explanation as to why conversion stopped after the reaction time exceeded 4 h.

The deactivation was probably due to material stuck within the zeolite framework, blocking the active sites. Since the catalytic activity of Hβ was restored after recalcination and the integrated material was burnt off.

A reaction with spent Hβ occurred to a small extent, so, it was decided to investigate other factors that may have contributed to the leveling off of product yield, after 4 h of the reaction.

3.2.3 Generation of methanol during a typical optimised reaction

Methanol was detected in the reaction mixture (by GC analysis) of a typical optimised reaction, after 4 h. A mechanism for the formation of methanol from DMM in the presence of an acidic catalyst has already been discussed in Section **3.1.5.2** in Part 1 of this Chapter, where it was suggested that methanol was the source of methylating agent in the formation of methylnaphthalene.

The amount of methanol generated during a typical optimised reaction, based on 82 % naphthalene conversion, was thought to be approximately 0.5 ml. It is known that methanol can be adsorbed by zeolites[10] (by interacting with zeolitic protons), therefore, it was decided to investigate the effect of methanol on the reaction.

3.2.3.1 Addition of methanol to an optimised reaction mixture

A series of reactions was carried out, and the amount of methanol added to the reaction mixture was varied from 0.5 ml to 10 ml. Reactions were carried out using the same procedure outlined in Section **3.1.11**, of Part 1 of this Chapter, i.e. under optimised conditions (4 h, 120 °C under self generated pressure) and with naphthalene (10 mmol) being stirred in an excess of DMM with 4 g of Hβ. The results are reported in Table 3.2.2. (It is important to note that the total amount of methanol in the system included the methanol generated during the course of the reaction, in addition to the methanol added at the start of the reaction).

The degree of reaction decreased when the amount of methanol added to the reaction mixture increased from 0.5 ml to 10 ml. An 82 % conversion of naphthalene was observed when the reaction proceeded without the addition of methanol at the start of the reaction. When 0.5 ml of methanol was added at the start of the reaction, the naphthalene conversion decreased to 75 %, and a 63 % conversion was observed on addition of 1 ml of methanol. A further decrease in conversion was observed when the amount of methanol added increased to 5 ml and 10 ml, 31 % conversion and 11 % conversion being observed, respectively.

Table 3.2.2: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Determining the effect of adding methanol to an optimised reaction mixture[a]

Methanol (ml)	0	0.5	1	2	5	10
Swansea experiment code	D60	D69	D68	D67	D66	D65
Naphthalene recovery (%)	18	25	37	54	69	89
Methylnaphthalenes (%)	0	0	0	0	0	0
MMN (%)	38	36	30	20	12	3
2/1 ratio	2.1	2.1	2.5	2.2	1.9	2.0
Bis(MM)N (%)	18	14	9	4	2	0
Total (%)	74	75	76	78	83	92

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol), methanol.

The yields of MMN and bis(MM)N also decreased when the volume of methanol added to the reaction mixture was increased. When 1 ml of methanol was added, the yields of MMN and bis(MM)N were 30 % and 9 % respectively. A 38 % yield of MMN and 18 % yield of bis(MM)N were observed with the reaction without additional methanol. A more significant decrease in product formation was observed when the volume of methanol added to the reaction increased to 5 ml and 10 ml, and the yield of MMN decreased to 12 % and 3 % respectively. The yield of bis(MM)N decreased to 2 % when 5 ml of methanol was added at the start of the reaction, and it was not observed in the presence of 10 ml of methanol.

The recovery of the material from the reaction mixture increased, as the volume of methanol added to the reaction mixture increased. This can be explained in terms of the proportional decrease in naphthalene conversion and yields of products

observed. If the degree of the reaction taking place was less, then one would also expect coke formation to be reduced, resulting in a better recovery of material from the reaction mixture.

The addition of methanol at the start of the reaction did not affect the selectivity of the reaction. A 2/1 ratio of 2.1 was observed when the reaction was carried out without additional methanol, compared to a 2/1 ratio of 2.0 when 10 ml of methanol was added to the reaction mixture.

In summary, the addition of methanol to the reaction mixture appeared to reduce the rate of reaction, resulting in a decrease in conversion and yield of products. This relationship was proportional, and the naphthalene conversion decreased as the volume of methanol added to the reaction mixture increased. This subsequently led to an increase in product recovery from the reaction mixture (suppressed coke formation due to reduced activity).

However, it is important to note that this effect was probably exaggerated, and was not a true reflection of what happens in a typical optimised reaction. Since the addition of methanol at the start of the reaction would limit product formation even before the reaction had started, whereas in a typical optimised reaction, the methanol would have been generated more steadily, as product formation increased with time. Therefore, the limiting effect of methanol would have been more gradual, and the reduction in product formation less pronounced.

Another factor that needs to be taken into consideration is that there was an increase in the total volume contained in the reactor (by adding methanol to the reaction), which could have effectively reduced the rate of reaction through dilution. However, one would not expect a small increase in volume between 0.5 ml and 10 ml to result in such a significant decrease in product formation, as observed. Therefore,

the limiting effect of methanol itself was almost certainly the main contributor to the decreased rate of reaction, rather than the increase in volume.

One can conclude that the presence of methanol in the reaction mixture did slow the reaction down but did not stop it completely.

3.2.4 Discussion

The combined effects of methanol, generated during the reaction (served to decrease the rate of reaction), and catalyst deactivation (by coke formation), offered a reasonable explanation for why the reaction did not proceed to completion, even under forcing conditions. Therefore, experiments were conducted, in an attempt to overcome these limiting factors, and improve the yields of MMN and bis(MM)N.

3.2.5 Attempts to overcome the limitations associated with the reaction

3.2.5.1 Removal of methanol from the reaction mixture

Firstly, it was decided to investigate methods of removing methanol from the system. These included removing methanol by chemical means, adding adsorbents to the reaction mixture, and by a physical method, removing methanol at the pump.

3.2.5.2 Adsorption of methanol by molecular sieves

Molecular sieves are synthetically produced zeolites that possess unique adsorbent properties[11]. They are used extensively in a wide range of commercial processes, including petroleum refining and petrochemical processes to reduce energy costs and industrial waste[12].

The structure of molecular sieves (discussed in more detail in Chapter 1) is based on crystalline metal aluminosilicates having a three dimensional interconnecting network of silica and alumina tetrahedra. Natural water of hydration is removed from this network by heating to produce uniform cavities which selectively adsorb molecules of a specific size. The rate at which molecules are

adsorbed or indeed if they are adsorbed at all is dependent on the size of the cavities. Thus molecules can be separated on the basis of size, with the adsorbents effectively acting as molecular sieves. Molecular sieves can also segregate molecules of the same size but different electrical characteristics or polarity. This is a very important property that is utilised in many applications including the recovery of radioactive ions from waste solution[13].

Molecular sieves are split into four primary generic forms including 3A, 4A, 5A and 13X, where the number represents the accessible pore size and the letter corresponds to the framework.

Type 3A molecular sieve is the potassium form of zeolite A (formula: $K_{12}[(AlO_2)_{12}(SiO_2)_{12}].nH_2O$) and the effective pore size corresponds to 3 Å. Therefore, type 3A adsorbs molecules that have a critical diameter less than 3 Å and excludes molecules with a diameter greater than 3 Å. The major applications of 3A molecular sieve include the commercial dehydration of unsaturated hydrocarbon streams and the drying of polar liquids such as methanol[14].

Type 4A molecular sieve is the sodium form of zeolite A (formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].nH_2O$). It has an effective pore opening of 4 Å, so that molecules of effective diameter greater than 4 Å, e.g. propane, are excluded. It is typically used in regenerable drying systems to remove water vapour and contaminants which have a critical diameter smaller than 4 Å[14].

Molecular sieve 5A corresponds to the calcium form of zeolite A (formula:$Ca_5Na[(AlO_2)_{12}(SiO_2)_{12}].nH_2O$) and has a pore diameter of 5 Å.13X is a modified form of the sodium zeolite (formula: $Na[(AlO_2)_{12}(SiO_2)_{12}].nH_2O$) and has an even larger pore diameter of 6.7 Å[14].

Therefore, it was hoped that if the appropriate molecular sieve was added to the reaction mixture, the methanol generated during the reaction would be adsorbed, thus encouraging further product formation. Methanol has a critical diameter of 4.4 Å; therefore, type 5A (pore size 5 Å) was chosen.

3.2.5.3 Addition of molecular sieve 5A to the reaction mixture

An initial reaction was carried out with naphthalene (10 mmol), dimethoxymethane (758 mmol) and molecular sieve 5A (4 g), under optimised conditions, to establish if the molecular sieve itself was catalytically active during the reaction. The same procedure was used as described in Section **3.1.11** of Part 1 of this Chapter and the results are reported in Table 3.2.3.

It was found that molecular sieve 5A exhibited limited catalytic activity during the reaction with MMN being observed in only a 2 % yield and bis(MM)N not being observed. A second reaction was carried out (under identical conditions), in which both molecular sieve 5 A (4 g) and Hβ (4 g) were added, to establish whether methanol generated during the reaction was adsorbed onto the molecular sieve. The results are also reported in Table 3.2.3.

Table 3.2.3: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Addition of molecular sieve 5A and Hβ under optimized conditions[a]

Catalyst	Hbeta[a]	5A[x]	Hbeta + 5A[y]
Swansea experiment code	D48	D62	D63
Naphthalene conversion (%)[b]	82	4	69
Naphthalene recovery (%)[b]	18	96	31
Methylnaphthalenes (%)[b]	0	0	0
MMN (%)[b]	38	2	31
2/1 ratio[c]	2.1	2.4	2.3
Bis(MM)N (%)[b]	18	0	16
Total (%)[b]	74	98	78

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).
[x] As [a] except: catalyst (4 g 5 A molecular sieve).
[y] As [a] except: catalyst (4 g Hβ, Si/Al 12.5 and 4 g 5 A molecular sieve).

On GC analysis of the reaction mixture after 4 h, it was found that methanol was still present, even though the reaction had proceeded in the presence of the molecular sieve. The quantity of methanol generated during the optimized reaction with Hβ or with Hβ and 5A was not measured quantitatively, therefore it was not known what amount of methanol, if any, was adsorbed by the molecular sieve. However, it was clear that a significant amount of methanol remained in the reaction mixture. The observations from the reactions with Hβ, and with Hβ and 5A molecular sieve, are discussed below.

The conversion decreased with both 5A and Hβ compared to the optimised reaction with Hβ alone, 69 % and 82 % conversion of naphthalene being observed respectively. The yields of products also decreased and MMN was observed in a 31 % yield when both molecular sieve 5A and Hβ were employed compared to a 38 % yield

with Hβ. In addition, the yield of bis(MM)N decreased from an 18 % yield with Hβ to a 16 % yield with Hβ and molecular sieve 5A.

Cation exchange between Hβ and the molecular sieve β (The framework of the Hβ contains large interconnected channels that allow mobile cations to be easily exchanged for other cations in the immediate environment) may have occurred to some extent, which could have affected the catalytic activity of Hβ by converting some of it to CaA slight increase in the recovery of material from the reaction mixture was observed when molecular sieve 5A and Hβ were employed together (78 % material recovered from reaction mixture) compared to the reaction that employed Hβ alone (74 % material recovered from reaction mixture).

The selectivity of the reaction was also marginally improved with a mixture of molecular sieve 5A and Hβ, compared to the selectivity of the reaction which employed Hβ alone (2/1 ratio of 2.3 and 2.1, respectively).

One can conclude that the incorporation of molecular sieve 5A in the reaction mixture did not serve to adsorb a significant proportion of the methanol generated during the reaction, and did not therefore, improve the reaction, in terms of increased product yield. Indeed, possibly because some ion-exchange took place between the two zeolites (Hβ and 5A), the reactivity of the system was reduced somewhat.

3.2.5.4 Removal of methanol at the pump

The adsorption of methanol by a chemical method was unsuccessful. Therefore, a reaction using a physical method to remove methanol was attempted. It was thought that if methanol was removed from the reaction mixture at the water pump after 4 h and the reaction restarted, conceivably, product formation would increase.

A typical optimized reaction was carried out, with dimethoxymethane (758 mmol) being reacted with naphthalene (10 mmol) in the presence of Hβ (4 g) under optimized conditions using the procedure described in Section **3.1.11** in Part 1 of this Chapter. After 4 h the reactor was cooled in an ice bath for 15 min and opened. The reaction mixture (including the zeolite) was transferred to a round bottomed flask and subjected to rotary evaporation to give a residue. A small sample of the residue was analysed by GC, and methanol was not detected. Dimethoxymethane was also removed at the pump, due to its high volatility.

The residue obtained, subsequent to evaporation (containing unreacted naphthalene, (methoxymethyl)naphthalene, bis((methoxymethyl)naphthalene) and spent zeolite), was put back into the reactor with fresh DMM (758 mmol), and stirred for a further 4 h at 120 °C (this reaction, will be referred to as **Reaction 2**).

The results of **Reaction 2** were compared to a typical 4 h optimized reaction, to determine if an increase in product yield was observed after the reaction was restarted, in the absence of methanol. The results are reported in Table 3.2.4.

Table 3.2.4: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Restarting the reaction subsequent to methanol removal at the pump, under optimised conditions.

	Optimised Reaction[a]	Reaction 2 Removal of Methanol[x]
Swansea experiment code	D48	RC1
Naphthalene recovery (%)	18	19
Methylnaphthalenes (%)	0	0
MMN (%)	38	32
2/1 ratio	2.1	2.1
Bis(MM)N (%)	18	17
Total (%)	74	68

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).
[x] As [a] except: removal of methanol and dimethoxymethane at the pump after 4 h, addition of fresh dimethoxymethane (57.6 g, 758 mmol) then further reaction for 4 h under the same conditions as described above.

The conversion observed in **Reaction 2** was almost the same as the conversion observed in a typical optimized reaction, with 81 % conversion of naphthalene compared to 82 % conversion of naphthalene, respectively.

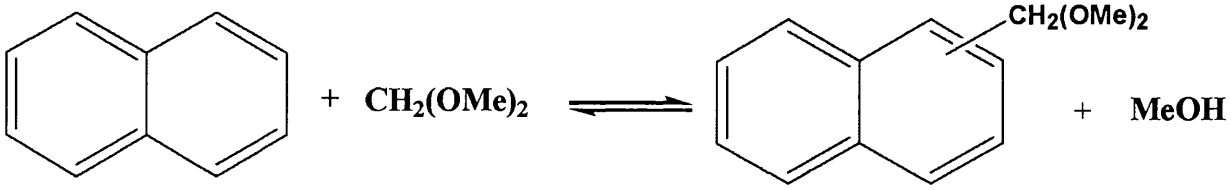
The yield of MMN decreased slightly, a 32 % yield of MMN being observed in **Reaction 2**, after the reaction was restarted subsequent to methanol removal, compared to 38 % in a typical optimized reaction. The yield of bis(MM)N also decreased, with a 17 % yield being observed in **Reaction 2** compared to an 18 % yield in a typical optimized reaction. The recovery of material from the reaction mixture decreased from 74 % in the optimized reaction to 68 % in **Reaction 2**. The selectivity was identical in **Reaction 2** and in the optimized reaction, with a 2/1 ratio of 2.1 being observed in both reactions.

The decrease in product yield in the recovery of material from the reaction mixture was probably due to further coke formation during the second stage when the reaction was restarted.

One can conclude that the product formation did not increase when the reaction was restarted in the absence of methanol. One would expect an increase in product yield if naphthalene, dimethoxymethane and active zeolite were present, in the absence of methanol. Therefore, this suggests that the deactivation of Hβ during the initial 4 h of the reaction prohibited the reaction proceeding further in the second stage, after methanol had been removed. Therefore it appeared that the overriding factor stopping naphthalene conversion after 4 h was the deactivation of the Hβ catalyst.

3.2.6 Establishing an equilibrium

Another possible effect that may have led to the leveling off of product yield was the generation of an equilibrium between reactants and products formed (as shown in **Reaction scheme 3.2.1**), which would be established after a certain time. Therefore, even under forcing conditions it would be difficult to push the reaction to completion.



Reaction scheme 3.2.1: Proposed equilibrium between reactants and products formed

Experiments were conducted to determine if such an equilibrium existed. A pure sample of MMN (1.72 g, 10 mmol) (synthesised via an authentic route, as

described in Section 3.5.4 in Section 1 of this chapter) was reacted with dimethoxymethane (758 mmol) with Hβ (4 g) and methanol (0.5 ml), under optimised conditions. If an equilibrium were to exist between reactants and products formed, naphthalene would be generated.

Reactions were carried out with both 1-MMN and 2-MMN using the procedure outlined in Section **3.1.11** of Part 1 of this Chapter, and the results are reported in Table 3.2.5. GC analysis of the product mixtures showed naphthalene was not generated; therefore, there was no evidence that supported a reverse reaction.

3.2.6.1 Selective di-substitution.

The results reported in Table 3.2.5 demonstrated the preferential di-substitution of 2-MMN over 1-MMN. This was reflected in the reaction incorporating 2-MMN, where bis(MM)N was observed in a 20 % yield, compared to the reaction with 1-MMN, where a second substitution was not observed and 1-MMN was recovered quantitatively. This was a significant observation, regarding the selectivity of the di-substituted isomers generated, in the reactions reported in Part 1 (3 isomers). If a second substitution of 2-MMN was exclusively favored over 1-MMN, the number of possible di-substituted isomers formed during the reaction would be reduced. Therefore, the probability of generating the desired 2,6-isomer was increased.

Table 3.2.5: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Establishing an equilibrium between naphthalene, dimethoxymethane, methanol and (methoxymethyl)naphthalene[a].

	1-MMN	2-MMN
Swansea experiment code	Eq-MeOH-1-MMN	Eq-MeOH-2-MMN
MMN Recovery (%)	100	78
Naphthalene (%)	0	0
Bis(MM)N (%)	0	20
Total (%)	100	98

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, Si/Al 12.5), dimethoxymethane (57.6 g, 758 mmol); (methoxymethyl)naphthalene (1.72 g 10 mmol), methanol (0.5 ml).

3.2.7 Attempts to overcome the deactivation of Hβ

The results set out in Table 3.2.1 clearly show that Hβ was deactivated during the course of the reaction, preventing a 100 % conversion of naphthalene. In view of this, reactions were carried out in an attempt to overcome the deactivation of Hβ, and increase conversion.

3.2.7.1 Addition of fresh Hβ after 4 h

As mentioned previously, reagents were still present in the reaction mixture after 4 h; therefore, addition of fresh Hβ after 4 h may overcome the deactivation of Hβ and restart the reaction.

In view of this, two analogous reactions were carried out, based on a typical optimized reaction except that further Hβ (4 g) was added after the 4 h. In the first reaction (**Reaction A**), spent Hβ was filtered at the pump prior to the addition of fresh Hβ, in the second reaction (**Reaction B**), spent Hβ was incorporated into the second stage with the additional fresh Hβ (to establish if spent Hβ had an affect on the second stage). These reactions were compared to a typical optimized reaction, to determine if

conversion increased on addition of fresh catalyst. The reactions are explained in more detail below.

3.2.7.2 Reaction A: Filtration of spent zeolite prior to the addition of fresh Hβ

Firstly, naphthalene (10 mmol) was stirred with dimethoxymethane (758 mmol) and Hβ (4 g) for 4 h at 120 ° C. After the given reaction time, the mini reactor was cooled in an ice bath for 15 min and then opened. The spent zeolite was filtered at the pump to give the mother liquor that comprised unreacted naphthalene, DMM, (methoxymethyl)naphthalene and bis(methoxymethyl)naphthalene. The mother liquor and additional, freshly calcined Hβ (4 g) were put back into the reactor, and stirred for a further 4 h at 120 ° C.

3.2.7.3 Reaction B: Incorporating spent zeolite in the second stage

The same procedure and reaction conditions were used as for **Reaction A**, except spent Hβ was incorporated into the second stage with the additional freshly calcined Hβ (4 g), thus avoiding the filtration process.

3.2.7.4 Analyses of Reaction A and Reaction B after 4 h and 8 h

The reaction mixtures of **Reaction A** and **Reaction B** were analysed after the initial 4 h period (prior to catalyst addition), and after the final reaction time of 8 h (subsequent to the addition of fresh zeolite). This allowed an accurate comparison of the conversion before and after the addition of fresh catalyst.

The mini reactors were cooled in an ice bath for 15 min after the initial 4 h reaction time and 8 h final reaction time, and then opened. The reaction mixtures were stirred mechanically, and aliquot samples (1 ml) were taken using a pipette. The liquid – solid mixture was drawn and released through the pipette several times, to ensure the sample was uniform and representative of the whole reaction mixture. The solution was filtered through a sinter funnel under gravity to separate the zeolite (to give a

filtrate). The zeolite was then washed with acetone (3 x 20 ml), and the washings were combined with the filtrate. The solution was made up to a known volume in a volumetric flask with acetone, and analysed by GC. The relative amounts of products and reagents were then calculated.

3.2.7.5 Limitations associated with the results calculated from aliquot samples

The results calculated from the aliquot samples after the initial stages of **Reaction A** and **Reaction B** did not correspond to each other, or to the results obtained from the 4 h optimised reaction. One would expect the results from the aliquot samples of **Reactions A** and **B** to be comparable to each other and to results from the mother liquor of the optimised reaction, because essentially the same reaction took place. This suggested that the aliquot samples were inaccurate and not representative of the whole reaction mixture.

For example, the yield of MMN calculated from the analysis of the aliquot sample taken from **Reaction A** after the initial 4 h period, at 58 %, was significantly higher than the yield of MMN (42 %) calculated from the analysis of the aliquot taken from **Reaction B** after the initial 4 h period.

In addition, the results calculated from the analysis of the aliquot samples after the final reaction time, in both **Reactions A** and **B**, did not correlate with the results calculated from the analysis of the final mother liquor of each respective reaction. This demonstrates that analyses of the same reaction mixture gave different results depending on whether an aliquot or the entire reaction mixture was used for analyses.

There is a risk of not getting a representative sample of solid (zeolite) and liquid (solution), so that if the proportions are different in the two phases the results will be misleading.

It was possible that products and reagents were adsorbed onto the surface of the zeolite, as well as in solution. Particular compounds may have been more strongly adsorbed onto the zeolite surface than others, and if the aliquot sample did not contain an equal solid to liquid ratio, the sample would conceivably contain more of one compound than another. This would reflect in the results obtained from the GC analysis of the aliquot samples.

Due to the unreliability of the results based on analysis of the aliquot samples, it was assumed that the results from a typical 4 h optimized reaction were a fair indication of the level of product formation in **Reaction A** and **Reaction B** after 4 h (essentially the same reaction, within experimental error), and these results are compared to the results obtained from the mother liquors of **Reaction A** and **Reaction B** after the final reaction time in Table 3.2.6.

Table 3.2.6: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Addition of fresh Hβ to the reaction mixture after 4 h[a]

	4 g *(Optimised reaction)*[a]	**4 g x 2** *(Separation of spent zeolite)*[x]	**4 g x 2** *(Incorporation of spent zeolite)*[y]
Swansea experiment code	**Single stage**	**Reaction A - 2 stages**	**Reaction B- 2 stages**
Naphthalene recovery (%)	**18**	**11**	**22**
Methylnaphthalenes (%)	**0**	**0**	**0**
MMN (%)	**38**	**36**	**39**
2/1 ratio	**2.2**	**1.3**	**1.6**
Bis(MM)N (%)	**18**	**21**	**18**
Total (%)	**74**	**68**	**79**

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

x As [a] except: Separation of spent zeolite, then: addition of catalyst (4 g Hβ, Si/Al 12.5) and stir for a further 4 h under the same conditions described above.

[y] As [a] except: Incorporation of spent zeolite, then: addition of catalyst (4 g Hβ, Si/Al 12.5) and stir for a further 4 h under the same conditions described above

3.2.8 Reaction A: Filtration of spent zeolite prior to addition of fresh Hβ

The results reported in Table 3.2.6 show how the conversion increased after the addition of fresh catalyst, with an 89 % conversion of naphthalene being observed in **Reaction A** (after 8 h), compared to an 82 % conversion of naphthalene observed after 4 h in a typical optimised reaction.

The yield of MMN after 8 h in **Reaction A** was slightly lower than observed after 4 h in the optimised reaction (36 % and 38 % respectively). However, the yield of bis(MM)N increased slightly, from 18 % after 4 h to 22 % after 8 h in **Reaction A**.

This suggested that MMN had reacted further with dimethoxymethane to give bis(MM)N on addition of the fresh catalyst.

The recovery of material from the reaction mixture in **Reaction A** was lower than the recovery of material from the reaction mixture in the optimised reaction (68 % and 74 % respectively). This was probably due to further coke formation during the extended reaction time in the presence of fresh Hβ.

In summary, it appeared that the reaction did restart and an increase in conversion was observed, subsequent to addition of fresh catalyst.

3.2.9 Reaction B: Incorporating both spent and fresh Hβ in the second stage

The results observed in **Reaction B** were not the same as the results observed in **Reaction A.** An increase in conversion was not observed following the addition of fresh catalyst after 4 h when the spent Hβ was left in the mixture.

A 78 % conversion of naphthalene was observed after the final reaction time in **Reaction B**, compared to an 82 % conversion of naphthalene observed after 4 h in the optimised reaction. The conversion in **Reaction B** was similar to that in the typical optimised reaction.

A 39 % yield of MMN was observed in **Reaction B** compared to a 38 % yield observed in the optimised reaction, and an 18 % yield of bis(MM)N was observed in both **Reaction B** and the 4 h optimised reaction. The recovery of material from the reaction mixture in **Reaction B** was actually higher, compared to the recovery of material from the reaction mixture in the 4 h optimised reaction (79 % and 74 %, respectively).

These results suggest the reaction did not restart on addition of fresh Hβ when the spent Hβ remained in the system. However, the differences between all these reactions were relatively small and these kinds of heterogeneous reactions are

notoriously difficult to reproduce consistently. Consequently, the results from **Reaction A** and **Reaction B** could be misleading.

3.2.10 Limitations of Reaction A and Reaction B

As mentioned previously, the results observed for the 4 h optimised reaction were assumed to be the same as would be observed in **Reaction A** and **Reaction B** after 4 h, as these reactions were essentially the same. However, since no two reactions will ever be exactly the same, the yields of the products formed after the first stages may have been slightly more or less than was assumed. Small increases in product formation would therefore be difficult to detect, and conclusions drawn from **Reaction A** and **Reaction B** would be only approximate.

Also, the concentrations of naphthalene in the second steps of **Reaction A** and **Reaction B** would have been lower, compared to the concentration of naphthalene at the start of the reactions. This was because around 70 % of naphthalene was used to generate new products during the initial 4 h of the reactions. Consequently, the rates of reaction in the first steps (initial 4 h) of **Reactions A** and **B**, would have been faster than the rates of reaction in the second steps of **Reactions A** and **B**. Therefore, the direct comparison of product yields after the first and second steps, in order to establish an increase in conversion, would not be ideal. For a reasonable comparison to be drawn, ideally, the concentration of naphthalene would constant throughout the whole reaction.

In conclusion, from **Reaction A** the reaction appeared to restart on addition of fresh catalyst after 4 h. However, the increase in the extent of reaction was relatively modest and therefore difficult to be sure about, due to the low concentration of naphthalene at the start of the second stage. Indeed, in Reaction B it was not even

evident that there was any further reaction. For these reasons a modified procedure was developed.

3.2.11 Modified reaction procedure

A modified reaction was carried out, in an attempt to overcome the limitations associated with **Reaction A** and **Reaction B** and hopefully to increase conversion.

To ensure a constant concentration of naphthalene (and rate of reaction) throughout the whole reaction, extra naphthalene (to replace that already converted, during the initial 4 h) was added to the reaction mixture after 4 h. Spent Hβ was not separated from the reaction mixture prior to the addition of fresh catalyst, as it was thought that lost material from the reaction mixture would be minimised by avoiding the filtration process.

The extent of reaction observed after the initial 4 h reaction time, was assumed to be the extent of reaction observed in a typical, 4 h, optimised reaction. Even though this was an estimation, it was thought to be more accurate than results that could be obtained from the analysis of aliquot samples, which were found to be misleading in **Reaction A** and **Reaction B**.

A reaction was carried out in which naphthalene (10 mmol) was reacted with an excess of DMM, in the presence of Hβ (4 g) for 4 h at 120 °C. The reactor was cooled in an ice bath for 15 min and then opened. Fresh Hβ (4 g) and additional naphthalene (6.9 mmol) were added to the reaction mixture and the reaction was stirred for a further 4 h at 120 °C. This reaction will be referred to as **Reaction C** and the results are reported in Table 3.2.7. Due to the additional naphthalene in the second stage of **Reaction C**, results are quoted in mmol. This is because one can not directly compare the percentage yields of products observed in the typical 4 h optimised

reaction with the percentage yields of products observed after 8 h in **Reaction C**, as the total amount of naphthalene in the reactions was different.

Table 3.2.7: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Effect of adding more Hβ and naphthalene to the reaction using the modified procedure[a]

	Typical 4 h Optimised Reaction[a]	Reaction C[x]
Swansea experiment code	Single stage	Reaction C
Total naphthalene employed (mmol)	10.0	16.9
Naphthalene recovery (mmol)	1.8	4.9
Methylnaphthalenes (mmol)	0	0
MMN (mmol)	3.8	5.3
2/1 ratio	2.2	1.6
Bis(MM)N (mmol)	1.8	2.4
Total (mmol)	7.4	12.6
Total (%)	74	74

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, Si/Al 12.5), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).
[x] **Initial stage:** As [a] .**Second stage:** Addition of catalyst (4 g Hβ, Si/Al 12.5) and naphthalene (0.88 g, 6.9 mmol), stirred for further 4 h, under the same conditions described above.

The results in Table 3.2.7 demonstrated that the reaction had definitely restarted when fresh zeolite and extra naphthalene were added to the reaction mixture after 4 h and an increase in product formation was observed. 5.3 mmol of MMN was observed after 8 h in Reaction C, compared to 3.8 mmol of MMN observed after 4 h in a typical optimised reaction. 2.4 mmol of bis(MM)N was observed in **Reaction C**, compared to 1.8 mmol of bis(MM)N observed in a typical reaction. The percentage material recovery from the reaction mixture was the same in **Reaction C**, after 8 h of reaction time, as in the typical, 4 h, optimised reaction, with 74 % of material accounted for in each reaction. A decreased selectivity was observed in **Reaction C,**

compared to the typical optimised reaction, 2/1 ratios of 2.2 and 1.6 being observed, respectively.

To conclude, it was shown the reaction restarted on addition of fresh catalyst and more naphthalene after 4 h, and a reasonable yield of MMN and bis(MM)N was observed. Therefore, there was nothing generated in the reaction mixture that quenched the reaction. It appeared that the problem was with the deactivation of the zeolite.

3.2.12 Further attempts to increase conversion with Hβ

3.2.12.1 Increasing the Si/Al ratio of Hβ under optimized conditions

It is known [16-18] that increasing the Si/Al ratio of a zeolite can lead to an increase in conversion (At higher Si/Al ratio there are fewer acid sites, but they are stronger). Therefore, reactions were carried out under optimized conditions, with different samples of Hβ, for which the Si/Al ratios were 12.5 and 37.5. The same procedure was used as described in Section **3.1.11** in Part 1 of this Chapter, and the results are reported in Table 3.2.8.

Table 3.2.8: ***Reaction of naphthalene and dimethoxymethane over Hβ:*** Varying the Si/Al ratio of Hβ under optimised conditions[a]

Si/Al ratio of Hbeta	12.5	37.5
Swansea experiment code	D48	D61
Naphthalene recovery (%)	18	33
Menaphthalenes (%)	0	<1
MMN (%)	38	34
2/1 ratio	2.2	1.7
Bis(MM)N (%)	18	14
Total (%)	74	82

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g Hβ, varying Si/Al ratio), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol)

The results reported in Table 3.2.8 illustrate that naphthalene conversion decreased when the Si/Al ratio of Hβ was increased from 12.5 to 37.5 (82 % and 67 % respectively). Product formation also decreased, and MMN was observed in a 38 % when the Si/Al ratio of Hβ was 12.5, compared to a 34 % yield, when the Si/Al ratio of Hβ was 37.5. In addition, the yield of bis(MM)N decreased from 18 % to 14 % when the Si/Al ratio of Hβ increased from 12.5 to 37.5, respectively. Furthermore, the selectivity of the reaction decreased on increasing the Si/Al ratio of Hβ, with a 2/1 ratio of 2.2 being observed when the Si/Al ratio of Hβ was 12.5 compared to a 2/1 ratio of 1.7 when the Si/Al ratio of Hβ was 37.5. One can conclude that increasing the Si/Al ratio of Hβ under optimized conditions did not increase the conversion or selectivity of the reaction. A probable explanation for the decrease in conversion is that fewer acid sites leads to a slower reaction.

Several avenues for increasing the conversion of naphthalene into MMN and bis(MM)N have been explored, and it has been shown that reasonable yields of MMN and bis(MM)N (38 % yield and 18 % yield, respectively) are observed under optimized conditions, with Hβ. Moreover, higher yields of MMN and bis(MM)N were observed on addition of fresh zeolite and more naphthalene after 4 h of reaction time.

In view of this, attention was focused on improving the selectivity of the reaction towards the favored 2-MMN isomer and further reactions were carried out in an attempt to increase the 2/1 ratio.

3.2.13 Attempts to increase selectivity under optimized conditions

Even though reasonable yields of MMN and bis(MM)N were observed with Hβ, the reaction was not very selective, with a 2/1 ratio of 2.2 being observed under optimized conditions (the selectivity of di-substituted products will be discussed at length in chapter 4).

Proton-form mordenite was found to be the most selective zeolite in the preliminary methoxymethylation reactions, when a 2/1 ratio of 12.9 was observed (unfortunately, this was coupled with only a 13 % conversion), compared to a 2/1 ratio of 1.9 with Hβ under the same conditions (these results are reported in Table 3.1.1, in Part 1 of this chapter).

Therefore, reactions were carried out with HM under the new modified conditions, in an attempt to improve the selectivity.

3.2.13.1 Application of HM to the optimized conditions

A reaction was carried out with HM (4 g, Si/Al: 10) under optimized conditions, using the procedure set out in Section **3.1.11** in Part 1 of this Chapter, and the results are compared to a reaction with Hβ under the same conditions in Table 3.2.9. * *The optimized reaction with zeolite Hβ was repeated 20 times and the results were shown to be reproducible within experimental error**.

Table 3.2.9: ***Reaction of naphthalene and dimethoxymethane over HM:*** Applying HM to the new optimised conditions[a].

	HM Original Conditions[a]	HM Optimised Conditions[a*]	HBeta Optimised Conditions[a*]
Swansea experiment code	D7	D62a	D48
Naphthalene recovery (%)	87	73	18
Methylnaphthalenes (%)	5	0	0
MMN (%)	4	26	38
2/1 ratio	12.9	3.0	2.2
Bis(MM)N (%)	0	0	18
Total (%)	96	99	74

[a] 18 h stirred mini reactor reaction at 150 °C under self generated pressure; catalyst (4 g, HM), naphthalene (1.28 g, 10 mmol), dimethoxymethane (6.08 g, 80 mmol) and cyclohexane as solvent (60 ml).
[a*] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

When HM was employed under the new optimised conditions, a 2/1 ratio of 3.0 was observed, compared to a 2/1 ratio of 2.2 when Hβ was employed. However, the conversion was lower at 27 % with HM, compared to an 82 % conversion with Hβ. The yield of MMN was lower with HM compared to Hβ, with 26 % and 38 %

yields of MMN being observed, respectively. In addition, bis(MM)N was not observed with HM under the new optimised conditions, whereas bis(MM)N was observed in an 18 % yield with Hβ. The biggest improvement observed when HM was employed under the new conditions compared to Hβ was the significant improvement of material recovery from the reaction mixture. With HM 99 % of material was recovered, compared to only 74 % of material being recovered from the reaction mixture with Hβ. This suggests that the channels within HM were not clogged with organic material, and therefore, HM maybe deactivated more slowly or to a lesser extent than Hβ. This would be an obvious advantage from an industrial viewpoint for the economics of the process (reusability of the zeolite).

Even though a significant decrease in conversion was observed when HM was employed under the optimised conditions, the increase in selectivity, coupled with the increase in recovery of material from the reaction mixture, illustrated that the reaction with HM had potential. Therefore, further reactions were carried out with HM in an attempt to improve conversion.

3.2.14 Attempts to increase the conversion with HM

3.2.14.1 Increasing the Si/Al of HM under optimised conditions

As mentioned earlier, it is known that increasing the Si/Al ratio of a zeolite in this type of reaction can result in an increase in conversion[16-18]. In view of this, the reaction carried out with HM (Si/Al ratio 10) under optimised conditions (using the experimental procedure set out in Section **3.1.11** in Part 1 of this Chapter) was compared with one with HM with a Si/Al ratio of 40. The results are reported in Table 3.2.10.

Table 3.2.10: ***Reaction of naphthalene and dimethoxymethane over HM:*** Varying the Si/Al ratio of HM under optimised conditions[a]

Si/ Al ratio of HM	10	40
Swansea experiment code	D62a	DMM+HM(40)4g
Naphthalene recovery (%)	73	30
Methylnaphthalenes (%)	0	0
MMN (%)	26	48
2/1 ratio	3.0	3.2
Bis(MM)N (%)	0	19
Total (%)	99	97

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g HM with varying Si/Al ratio), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

The results in Table 3.2.10 demonstrate how the conversion increased significantly (27 % and 70 % conversion, respectively), when the Si/Al ratio of HM was increased from 10 to 40. In addition, the yield of MMN increased from 26 % to 48 % on increasing the Si/Al ratio from 10 to 40. The most significant improvement observed when the Si/Al ratio of HM was increased, was the formation of bis(MM)N, which was observed in a 19 % yield with HM Si/Al 40, whereas it was not observed with HM Si/Al 10. The selectivity of the reaction also increased somewhat, with a 2/1 ratio of 3.2 being observed with HM Si/Al 40, compared to a 2/1 ratio of 3.0 with HM Si/Al 10. This could have resulted from slightly different rate constants for conversion of the two MMN isomers into bis(MM)N, which was observed with HM Si/Al 10.

To summarise, the conversion and selectivity increased when the Si/Al ratio of HM was increased from 10 to 40. Furthermore, the selectivities and yields of MMN

and bis(MM)N observed with HM Si/Al 40, were higher than those observed in the analogous reaction with Hβ, under the modified reaction conditions. (A 48 % yield of MMN and 19 % yield of bis(MM)N was observed with HM Si/Al 40, compared to a 38 % yield of MMN and 18 % yield of bis(MM)N with Hβ. In addition, a 2/1 ratio of 3.2 was observed with HM Si/Al 40 compared to a 2/1 ratio of 2.2 with Hβ under the same conditions).These results were very encouraging and the study of the HM catalysed reaction under the new conditions was continued.

3.2.14.2 Increasing the amount of HM (Si/Al: 40) under optimised conditions

In an attempt to increase conversion even further, the amount of catalyst was increased. A reaction was carried out under the new optimised conditions, and the amount of HM Si/Al 40 was increased from 4 g to 8 g (using the same procedure as outlined in Section **3.1.11** in Part 1 of this Chapter). The results are reported in Table 3.2.11.

The reaction proceeded further, and the naphthalene conversion increased from 70 % to 91 %, when the amount of HM was increased from 4 g to 8 g. The yield of MMN decreased slightly, with a 48 % yield of MMN being observed with 4 g of HM, compared to a 45 % yield of MMN with 8 g of HM. The yield of bis(MM)N increased significantly, and a 19 % yield was observed with 4 g of HM, compared to a 45 % yield with 8 g of HM. Furthermore, almost all the material from the reaction mixture was accounted for, suggesting that coke was not formed to any substantial extent.

These results show that the decrease in yield of MMN, observed when the amount of HM was increased, was due to further reaction of MMN with dimethoxymethane to generate more bis(MM)N.

Table 3.2.11: ***Reaction of naphthalene and dimethoxymethane over HM:*** Increasing the amount of HM Si/Al 40 under the new optimised conditions[a]

Amount of HM (40)	4 g	8 g
Swansea experiment code	DMM+HM(40)4g	DMM+HM(40)8g
Naphthalene recovery (%)	30	9
Methylnaphthalenes (%)	0	0
MMN (%)	48	45
2/1 ratio	3.2	3.0
Bis(MM)N (%)	19	45
Total (%)	97	99

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (HM Si/Al 40), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

The only disadvantage observed when the amount of catalyst was increased, was a decrease in the selectivity of the reaction. A 2/1 ratio of 3.2 was observed with 4 g of HM, compared to a 2/1 ratio of 3.0 with 8 g of HM. Perhaps these small differences are not significant. However, was still more selective than the reaction with Hβ under optimised conditions, where a 2/1 ratio of 2.2 was observed.

3.2.15 Further attempts to increase conversion and selectivity with HM

3.2.15.1 Applying dealuminated HM (Si/Al: 40) under optimised conditions.

The previous experiments, reported in Table 3.2.10, showed how conversion and selectivity were increased when the Si/Al ratio of HM was increased, under optimised conditions. The framework Si/Al ratio of zeolites can be further controlled by dealumination of the catalyst, which involves the removal of aluminium from the zeolite framework sites, therefore decreasing the framework Si/Al ratio. Consequently, the net number of Bronsted sites decreases, but the acid strength of the

remaining Bronsted sites is enhanced[15] (since only a small number of aluminium cations are placed in the next nearest neighbour positions). Dealumination of the zeolite catalyst also generates mesopores which help to overcome barriers associated with diffusion in the zeolite micropores. Therefore, dealuminated samples of HM Si/Al 40 were prepared, and applied to the new modified conditions, in the hope of improving the conversion and selectivity.

HM Si/Al 40 was dealuminated by acid leaching, where it was essentially stirred with hydrochloric acid (HCl) at high temperature for a fixed period of time. Two dealuminated samples were prepared, in which HM (Si/Al 40) was treated with 4 M HCl (**Sample A**) and 8 M HCl (**Sample B**). The Si/Al ratios, and the volume of mesopores created, were not determined following dealumination.

Reactions were carried out with **Sample A** and **Sample B** (4 g of each dealuminated sample were used as stocks were low), using the same procedure set out in Section **3.1.11** in Part 1 of this Chapter, under optimised conditions, and compared with the non-dealuminated HM (Si/Al 40). The results are reported in Table 3.2.12.

Table 3.2.12: ***Reaction of naphthalene and dimethoxymethane over HM:*** Application of dealuminated HM (40) under optimized conditions[a]

Catalyst	HM (40)	HM (Sample A)	HM (Sample B)
Swansea experiment code	DMM+HM(40)4g	D100	D102
Naphthalene recovery (%)	30	85	83
Methylnaphthalenes (%)	0	0	0
MMN (%)	48	11	12
2/1 ratio	3.2	3.2	4.8
Bis(MM)N (%)	19	0	0
Total (%)	97	96	95

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g HM), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

A significant decrease in conversion was observed with **Sample A,** compared to non-dealuminated HM, with conversions of 15 % and 70 % being observed, respectively. The yield of MMN also decreased, and a 11 % yield of MMN was observed with **Sample A,** compared to a 48 % yield of MMN with non dealuminated HM. In addition, bis(MM)N was not observed with dealuminated **Sample A**, whereas a 19 % yield of bis(MM)N was observed, in the analogous reaction with non dealuminated HM. The selectivity was unaffected, with a 2/1 ratio of 3.2 being observed for both reactions.

A decrease in conversion was also observed with **Sample B**, compared to the non-dealuminated sample, with a conversion of 17 % for **Sample B** and 70 % for the non-dealuminated sample. MMN also decreased, with a 12 % being observed with **Sample B** and 48 with the non-dealuminated sample. Once again, bis(MM)N was not

generated. The selectivity increased when dealuminated **Sample B** was employed, and a 2/1 ratio of 4.8 was observed, compared to a 2/1 ratio of 3.2 with nondealuminated HM.

The decrease in conversion observed with dealuminated **Sample A** and **Sample B** suggested that fewer acid sites remained in the zeolite, due to a significant proportion of aluminium being removed. Although stronger acid sites are present, if significant aluminium is removed the observed effect would be reduced activity due to significantly fewer sites. These results suggest that there is an optimum Si/Al ratio for HM, in order to achieve maximum conversion of naphthalene into MMN and bis(MM)N.

3.2.16 General discussion

An equilibrium between the reactants and the products formed was ruled out, and there appeared to be two contributing factors, that stopped the conversion after 4 h.

1. Deactivation of Hβ, by non retractable organic material that blocked the active sites of the catalyst.
2. The generation of methanol during the reaction, which decreased the rate of reaction.

Other significant observations included:

1. Addition of fresh Hβ and more naphthalene after 4 h restarted the reaction and increased conversion, essentially overcoming the deactivation.
2. Broadly comparable conversion and better selectivity were observed when HM (Si/Al 40) was applied to the optimized conditions established for Hβ, but the total recovery of material was better, suggesting that much less coke was produced in this case. Furthermore, use of a larger quantity of the HM zeolite resulted in higher yield while retaining the better selectivity.

3.2.17 Summary and Conclusions

Establishing why conversion stopped after 4 h:

Initial experiments were conducted in an attempt to determine why conversion stopped after 4 h. It was found that Hβ was deactivated by organic material stuck within the zeolite framework, which may have blocked the pore openings, therefore reducing the catalytic activity of the Hβ. It was also found that the activity of spent Hβ was restored after recalcination at 550 °C for 24 h.

Methanol, generated during the course of the reaction (0.5 ml in a typical optimized reaction, based on 82 % conversion of naphthalene), also had a limiting effect, and it was found to decrease the rate of reaction. A reaction was carried out in an attempt to increase conversion, and methanol was removed after 4 h. However, no significant increase in conversion was observed.

A reaction was conducted that ruled out an equilibrium between the reactants and products formed. Therefore, the major factor causing the conversion to stop after 4 h was deactivation of Hβ. Thus, the focus was turned towards overcoming the deactivation and increasing conversion.

Attempts to increase conversion with Hβ:

When fresh Hβ and more naphthalene were added to the reaction mixture after 4 h, the reaction restarted, and conversion increased, essentially overcoming deactivation. A reaction was carried out with Hβ having a higher Si/Al ratio (37.5), but the conversion and selectivity decreased.

Attempts to increase selectivity

Most avenues to improve conversion with Hβ had been investigated, therefore attention was focused on improving the selectivity. HM was the most selective zeolite in the initial methoxymethylation reactions, therefore, in an attempt to increase selectivity, a reaction was carried out with HM under the optimised conditions set out for Hβ.

Applying HM to the new optimised conditions:

The selectivity of the reaction increased when HM was employed under the new optimised conditions. A 2/1 ratio of 3.0 was observed with HM, compared to a 2/1 ratio of 2.2 with Hβ. However, the conversion decreased, a 27 % conversion being observed with HM compared to 82 % conversion with Hβ. The main improvement with HM was that nearly all the material from the reaction mixture was recovered, while only 74 % of material was recovered from the reaction mixture with Hβ.

Increasing conversion with HM under new optimised conditions:

Increasing the Si/Al ratio of HM

On increasing the Si/Al ratio of HM from 10 to 40, the conversion increased significantly from 27 % to 70 %. The selectivity of the reaction also increased, and a 2/1 ratio of 3.2 was observed with HM Si/Al ratio 40, compared to a 2/1 ratio of 3.0 observed with HM Si/Al ratio 10.

Increasing the amount of HM Si/Al 40

When the amount of HM Si/Al 40 was increased from 4 g to 8 g, the conversion increased even further (91 % conversion). The selectivity decreased slightly, and a 2/1 ratio of 3.0 was observed.

Application of dealuminated HM to the new conditions

Dealuminated HM was prepared and applied to the optimized conditions, in an attempt to improve conversion. The selectivity increased, and a 2/1 ratio of 4.8 was observed when HM dealuminated with 8 M HCl was used. However, the reaction occurred to a lesser extent, with only a 12 % yield of MMN being observed, compared to a 48 % yield of MMN and 19 % of bis(MM)N with non-dealuminated HM Si/Al 40 under the same conditions. The decrease in conversion was attributed to large amounts of aluminium being removed from the framework.

Comparing HM and Hβ under optimized conditions

A higher conversion (90 %) was achieved with HM (8 g, Si/Al 40), compared to Hβ (82 %) (4 g, Si/Al 12.5) under optimized conditions. The selectivity was also higher with HM (8 g, Si/Al 40) compared to Hβ (4 g, Si/Al 12.5) under optimized conditions, with 2/1 ratios of 3.0 and 2.2 being observed, respectively. Almost all the material from the reaction mixture was recovered with HM (8 g, Si/Al 40), while only 74 % of material was recovered from the reaction mixture with Hβ (4 g, Si/Al 12.5).

In conclusion, the main reason why conversion stopped after 4 h, was due to the deactivation of Hβ. Conversion was increased when fresh Hβ and more naphthalene were added to the reaction mixture after 4 h. Significantly, HM was found to be superior to Hβ in the methoxymethyaltion of naphthalene, in terms of material recovery and selectivity. It was conceivable that 100 % conversion could be achieved, to give the maximum yield of MMN and bis(MM)N, if the reaction with HM was optimized further (e.g. increase in reaction time, increase in catalyst amount).

The next section of work involves the isolation, and characterisation of bis(MM)N isomers.

3.2.18 Experimental

The reaction procedure was identical to that set out in Section **3.1.11** in Part 1 of this Chapter. Any exceptions are described in the footnotes under the relevant results table. GC analysis was identical to that described in Section **3.1.14** in Part 1 of this Chapter.

3.2.18.1 Dealumination of the HM catalyst by acid leaching

HM (16.0 g, Si/Al 40) was calcined at 550 °C for 24 h prior to dealumination. **Sample A** was obtained by stirring HM (40) (8.0 g) with 4 M HCl (200 ml) at 85 °C for 24 h, in a round bottomed flask fitted with a reflux condenser. **Sample B** was obtained by stirring HM (40) (8.0 g) with 8 M HCl (200 ml) under the same conditions. The catalyst was filtered and thoroughly washed with distilled water until the washings were chloride free (tested with silver nitrate, $AgNO_3$). **Samples A** and **B** were calcined at 550 °C for 24 h prior to experimentation.

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Chapter 3, Part 3

Characterisation of bis(MM)N isomers

3.3.1 Introduction

In the zeolite catalysed reactions of naphthalene and dimethoxymethane reported in Part 1 and Part 2 of this Chapter, several isomers of bis(MM)N were observed.

In the methoxymethylation of naphthalene over Hβ an 18 % yield of bis(MM)N was observed, under optimised conditions (naphthalene (10 mmol) was stirred with DMM (758 mmol) and Hβ (Si/Al 12.5, 4 g), for 4 h at 120 °C). Three isomers of bis(MM)N were observed (3 compounds corresponding to molecular weight 216 by GCMS analysis), with retention times of 39.4 (4 %), 44.1 (2 %) and 44.3 min (12 % yield) by GC analysis using the standard conditions.

In the methoxymethylation of naphthalene over HM a 45 % yield of bis(MM)N was observed, under optimised conditions (naphthalene (10 mmol) was stirred with DMM (758 mmol) and HM (Si/Al 40, 8 g), for 4 h at 120 °C). Two isomers of bis(MM)N were observed (2 compounds corresponding to molecular weight 216 by GCMS analysis), with retention times of 44.1 min (3 % yield) and 44.3 min (42 % yield) by GC analysis. The major isomer of bis(MM)N observed in the methoxymethylation of naphthalene over both Hβ and HM had a retention time of 44.3 min.

3.3.2 Characterisation of bis(MM)N isomers

3.3.2.1 Ruling out three bis(MM)N isomers

Reactions carried out previously in Part 2 of this Chapter indicated that the bis(MM)N isomers observed in the methoxymethylation of naphthalene over HM or Hβ were derived from 2-MMN as opposed to 1-MMN, thus ruling out three out of a possible ten isomers. This is because the potential bis(MM)N isomers generated during the reaction were dependent on the initial mono methoxymethylation products

(Section 3.1.5, Part 1, Chapter 3). A mixture of 1-MMN and 2-MMN was observed in a typical optimised reaction of naphthalene and dimethoxymethane over Hβ or HM; therefore, one would expect that the isomers observed could have been any of the possible 10 isomers of bis(MM)N. However, it was shown in Part 2 of this Chapter (Table 3.2.5) that in the second methoxymethylation reaction, 1-MMN was less reactive than 2-MMN.

Experiments were carried out in an attempt to establish if an equilibrium existed between reactants and products (and determine if this was the reason why the reaction did not reach completion even under forcing conditions). Reactions were carried out with pure samples of **1-MMN** and **2-MMN** with dimethoxymethane, Hβ and methanol.

There was no evidence that supported a reverse reaction (naphthalene was not detected in the reaction mixture after 4 h), but it was shown that 1-MMN did not react further with dimethoxymethane in the presence of Hβ to give bis(MM)N. Conversely, 2-MMN reacted further with dimethoxymethane, and a bis(MM)N mixture was observed in 20 % yield. Three isomers of bis(MM)N were detected by GCMS, with retention times of 39.4 min (5 % yield), 44.1 min (2 % yield) and 44.3 min (13 % yield).

It was noted that the isomers observed in the optimised reactions of dimethoxymethane and naphthalene over HM and Hβ described in Section **3.3.1,** corresponded to the isomers observed in the attempted equilibrium reaction with 2-MMN and dimethoxymethane. This suggests that the bis(MM)N isomers observed in the methoxymethylation of naphthalene over HM or Hβ were derived from 2-MMN and not 1-MMN.

Consequently, the potential number of bis(MM)N isomers that could have been generated was reduced, as 3 out of the possible 10 isomers of bis(MM)N would be ruled. These were; **1,4-, 1,5-**, and **1,8-** bis(MM)N, since these could only be observed in the methoxymethylation of 1-MMN. In view of this, one would predict that the isomers of bis(MM)N observed in the methoxymethylation of naphthalene over Hβ or HM could conceivably be **1,2-, 1,3-, 1,6-, 1,7-, 2,3-, 2,7-,** or **2,6-** bis(MM)N.

3.3.3 Attempts to isolate and characterise bis(MM)N isomers

3.3.3.1 Attempts to separate bis(MM)N isomers from the crude mixture in the reaction of dimethoxymethane and naphthalene over Hβ *(three bis(MM)N isomers)*

Firstly, the separation of the bis(MM)N isomers was attempted by column chromatography. A sample of crude reaction mixture (*brown oil containing; naphthalene, 1-MMN, 2-MMN and three bis(MM)N isomers*) was loaded onto the column and eluted with hexane: diethyl ether, in a 90:10 ratio. The bis(MM)N isomers were separated from the crude mixture, but the separation of each bis(MM)N isomer from the others was unsuccessful.

The mixture of the three bis(MM)N isomers (brown oil) was then subjected to further column chromatography, in an attempt to isolate each isomer. Again, the mixture was loaded onto the column and eluted with hexane: diethyl ether, in a 90:10 ratio. Due to the similar physical properties of the bis(MM)N isomers, however, a good separation was still not achieved.

The mixture of the three isomers was then subjected to reduced pressure Kugelröhr distillation. White crystals were collected in the distilled fraction, corresponding to the isomer with retention time 44.3 min (major isomer). Further

attempts to isolate the two remaining bis(MM)N isomers using reduced pressure distillation of the residue were unsuccessful.

3.3.3.2 Attempts to separate bis(MM)N isomers from the crude mixture in the reaction of dimethoxymethane and naphthalene over HM *(two bis(MM)N isomers).*

The crude mixture (brown oil containing naphthalene, 1-MMN, 2-MMN and two bis(MM)N isomers) was subjected to column chromatography (as described in Section **3.3.3.1**), and the bis(MM)N isomers were separated from the other components in the crude mixture. Attempts to separate the individual bis(MM)N isomers by column chromatography were, however, again unsuccessful.

The mixture of bis(MM)N isomers was then subjected to reduced pressure Kugelröhr distillation. White crystals were again collected, corresponding to the bis(MM)N isomer with retention time 44.3 min (major isomer). Unfortunately, the bis(MM)N isomer with retention time 44.1 min was not separated in pure form from the mixture.

3.3.4 Characterisation of bis(MM)N isomer with a retention time of 44.3 min

3.3.4.1 NMR analysis

In the ^{1}H NMR spectrum of the bis(MM)N isomer with a retention time of 44.3 min, two signals were observed in the aliphatic region, a singlet at δ 3.55 integrating for six protons, and a singlet at δ 4.55 integrating for four protons, corresponding to two CH_3 groups and two CH_2 groups of the two methoxymethyl substituents.

The fact that only two signals were observed in the aliphatic region suggests that the isomer was symmetrical, thus making the protons of the CH_2 and CH_3 groups of the methoxymethyl groups equivalent. If the isomer was not symmetrical, one

would expect four signals; one signal for each of the CH_2 groups and one signal for each of the CH_3 groups.

Three signals were observed in the aromatic region, a doublet at δ 7.45 integrating for two protons, a singlet at δ 7.70 integrating for two protons and a doublet at δ 7.75 integrating for two protons, corresponding to the six aromatic protons of the naphthalene ring. These signals also suggested that the isomer was symmetrical, and that three pairs of the aromatic protons were equivalent, (to give three signals in the aromatic region each integrating for two protons).

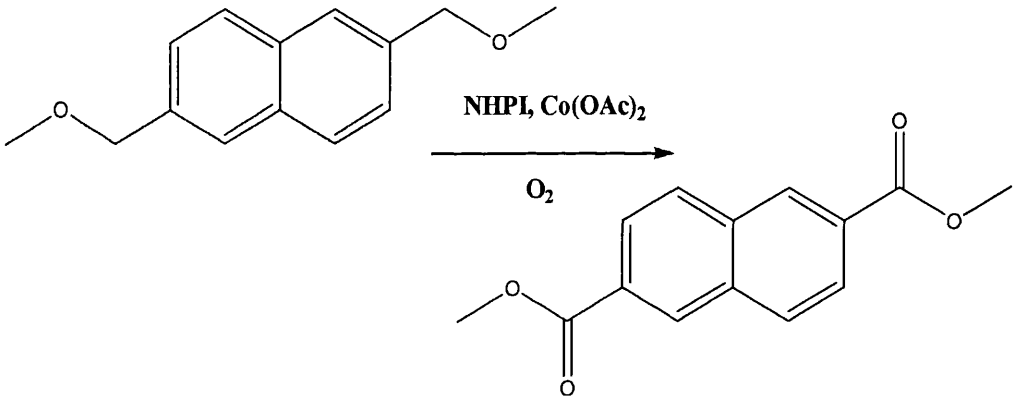
The coupling pattern observed in the aromatic region was characteristic of either a **2,6-** disubstituted naphthalene ring or a **2,7-** disubstituted naphthalene ring (both isomers would give the same NMR pattern). Therefore, it was impossible to determine if the isomer with retention time 44.3 min corresponded to 2,6-bis(MM)N or 2,7-bis(MM)N using NMR analysis.

In an attempt to determine if the isomer corresponded to 2,6-bis(MM)N or 2,7-bis(MM)N, a pure sample was sent away to DPT for further investigation.

3.3.4.2 Oxidation of isolated bis(MM)N isomer (retention time 44.3 min) –

Carried out by Dr Simon Roberts at DPT

A sample of the isolated bis(MM)N isomer was sent to Davy Process Technology and an oxidation reaction was carried out **(Reaction scheme 3.3.1)**, under conditions similar to those described in **US patent 6037477**. Bis(MM)N (200 mmol) was oxidised using NHPI (*N*-hydroxyphthalimide) catalyst (20 mmol), in acetic acid (30 mmol), with Co (II) acetate ($Co(OAc)_2$, 15 mmol) as promoter, and pure oxygen (1 bar, balloon fed) as the oxidant, at 25 °C for 20 h.



Reaction scheme 3.3.1 Expected oxidation product if major isomer was 2,6-bis(MM)N.

From GC, GCMS and authentic samples of dimethyl-2,6-naphthalenedicarboxylate (**2,6-NDC**) and 2,6-naphthalenedicarboxylic acid (**2,6-NDA**) (from Aldrich), DPT were able to determine qualitatively the products of the reaction. 2,6-NDC as well as a number of intermediates were identified, including insoluble 2,6-NDA which was the major product of the reaction.

Quantitative data were not obtained, only qualitative due to the difficulty in quantifying/analysing the insoluble acid. However, it was clear that the separated isomer was the 2,6 isomer which was therefore the dominant isomer in the product mixture.

The oxidation reaction was not performed to completion under the mild reaction conditions employed (25 °C, 1 bar), but, it was conceivable that the reaction could go to completion under more forcing conditions (longer reaction time, elevated temperature and increased reactants/promoter).

One can conclude that the major isomer of bis(MM)N, observed in the methoxymethylation of naphthalene with HM or Hβ (retention time 44.3 min), was the desired **2,6-bis(MM)N** isomer.

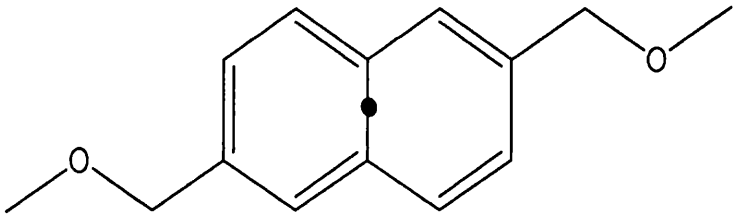


Figure 3.3.1: Diagram of 2,6-bis(MM)N illustrating the centre of symmetry

3.3.5 Characterisation of bis(MM)N isomers with retention time of 44.1 min

In an attempt to determine the structure of the bis(MM)N isomer with retention time 44.1 min, the ^{1}H NMR spectrum of a mixture of 2,6-bis(MM)N and the bis(MM)N isomer with retention time 44.1 min was carried out. The mixture of isomers isolated from the crude product of the reaction of dimethoxymethane and naphthalene over HM (Section **3.3.3.2**) was used for the analysis

The NMR spectrum of 2,6-bis(MM)N had already been determined (Section **3.3.4.1**), therefore the structure of the unknown isomer could be deduced by

eliminating the peaks that corresponded to 2,6-bis(MM)N from the NMR spectrum of the mixture.

3.3.5.1 NMR analysis of a mixture of 2,6-bis(MM)N and bis(MM)N isomer with retention time 44.1 min

In the aliphatic region of the 1H NMR spectrum of the mixture of bis(MM)N isomers, only two signals were observed; a singlet at δ 3.55 integrating for six protons, and a singlet at δ 4.55 integrating for four protons, corresponding to two CH_3 groups and two CH_2 groups of the methoxymethyl substituents. These were identical to the signals observed for pure 2,6-bis(MM)N.

The fact that only two signals were observed in the aliphatic region suggests that the second isomer has identical chemical shifts in the aliphatic region to those of 2,6-bis(MM)N. This suggests that the aliphatic proton chemical shifts are not very sensitive to the different nature of the bis(MM)N isomers, so that no firm conclusions can be drawn.

In the aromatic region, three signals were observed; a doublet at δ 7.45 integrating for two protons, a singlet at δ 7.70 integrating for two protons and a doublet at δ 7.75 integrating for two protons, again corresponding exactly to the protons of the naphthalene rings in pure 2,6-bis(MM)N. Although the peaks for the minor isomer were expected to be small (since the yields of major and minor isomers were 42 % and 3 %, respectively, the coupling patterns for 1,2-, 1,3-, 2,3-, 1,6- and 1,7- disubstituted isomers were expected to be very different from that of the 2,6-isomer. Therefore, it was expected that these isomers would at least be visible in the ^{1}H NMR spectrum), failure to observed any additional signals compared to the spectrum of 2,6-bis(MM)N therefore suggested that the minor isomer was

2,7-bis(MM)N, whose 1H NMR coupling pattern would be identical to that of 2,6-bis(MM)N and whose chemical shifts might also be very similar.

As already mentioned, one would expect the NMR spectra of 2,6- and 2,7-bis(MM)N to be very similar, and the fact that 2,6-bis(MM)N was known to correspond to the isomer with retention time 44.3 min, indicated that the isomer with retention time 44.1 min probably corresponded to 2,7-bis(MM)N.

Therefore, one can conclude that the bis(MM)N isomer with retention time 44.1 min probably corresponded to **2,7-bis(MM)N** and exhibited a ^{1}H NMR spectrum virtually identical to that of the 2,6-bis(MM)N isomer.

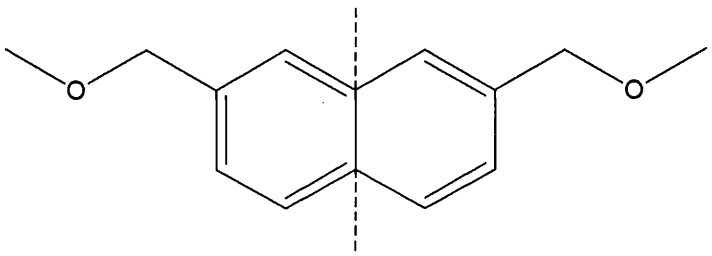


Figure 3.3.2: Diagram of 2,7-bis(MM)N illustrating a planeof symmetry

3.3.6 Characterisation of bis(MM)N isomer with retention time of 39.4 min

3.3.6.1 NMR analysis of a mixture of 2,6-bis(MM)N, 2,7-bis(MM)N and the bis(MM)N isomer with retention time 39.4 min

The bis(MM)N isomer with retention time 39.4 min was not isolated pure from any reaction mixture, thus a pure sample was not available for characterisation. Therefore, the ^{1}H NMR spectrum of a mixture of 2,6-bis(MM)N, 2,7-bis(MM)N and the unknown bis(MM)N isomer (retention time 39.4 min) was carried out. The mixture of isomers isolated from the crude reaction from the reaction of

dimethoxymethane and naphthalene over Hβ (Section **3.3.3.1**) was used for the mixed NMR analysis. Since the isomer proportions in this mixture were 4 % (retention time 39.4 min), 2 % (44.1 min) and 12 % (44.3 min), and since the spectra of the latter two isomers were virtually the same, the integral ratios per proton for the 39.4 min isomer were expected to be about 30 % of the intensities of those for the other combined isomers.

The NMR spectrum of 2,6-bis(MM)N and 2,7-bis(MM)N had already been determined (Section **3.3.4.1** and Section **3.3.5.1,** respectively), therefore it was hoped that the structure of the isomer with retention time 39.4 min could be deduced by eliminating the peaks in the NMR spectrum that corresponded to 2,6-bis(MM)N and 2,7-bis(MM)N.

In the aliphatic region, two signals were observed; a singlet at δ 3.55 (corresponding to the CH_3 groups in the methoxymethyl substituents of the three isomers), and a singlet at δ 4.55 (corresponding to the CH_2 groups in the methoxymethyl substituents of the three isomers). This suggested that the third isomer also had identical aliphatic signals, again demonstrating the lack of sensitivity of the aliphatic signals to isomer structure.

In the aromatic region there were four signals around δ 7.77 (m), δ 7.72 (s), δ 7.70 (s) and δ 7.45 (m), which integrated in the approximate ratio of 6:2:4:6. Given that the ratio of isomers in the mixture was 4:2:12 and the latter two isomers (2,7- and 2,6- respectively) show virtually identical ^1H NMR signals, it seemed that there were just three signals for the unknown isomer at around, δ 7.77, δ 7.72 (s) and δ 7.45. The signals at around δ 7.77 and δ 7.45 overlapped with those of the other isomers.

The only signal that was useful in helping the assignment was the singlet at δ 7.72. This signal did not correspond to either 2,6- or 2,7-bis(MM)N and therefore clearly corresponded to the unknown isomer, and it must have corresponded to two protons within that isomer. The only other isomer possible which would exhibit a two proton singlet would be 2,3-bis(methoxymethyl)naphthalene (**Figure 3.3.3**)

From the integrations of the signals at around δ 7.77 and δ 7.45, it was also clear that the other signals for the new isomer also integrated for two protons each, suggesting that there was a total of three equal intensity signals, which is consistent with the symmetrical structure of the 2,3-isomer.

If the isomer was non-symmetrical there would not have been any equivalent protons, consequently twice as many signals should have been observed. In view of this, several isomers could be ruled out including; 1,2-, 1,3-, 1,6- and 1,7-bis(MM)N. Therefore one can deduce that the third isomer, with retention time 39.4 min, actually corresponded to **2,3-bis(MM)N**.

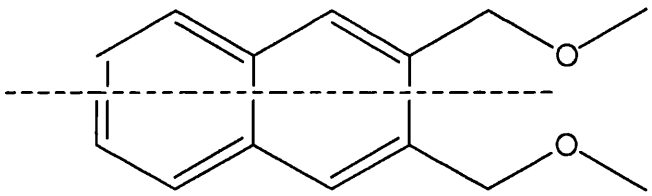


Figure 3.3.3: Diagram of 2,3-bis(MM)N illustrating a plane of symmetry.

3.3.7 Establishing the selectivity of the optimised methoxymethylation reaction of naphthalene over HM and Hβ towards the favoured 2,6-bis(MM)N isomer.

The selectivity of the optimised methoxymethylation reactions of naphthalene over HM and Hβ could be determined by establishing the ratios of the 2,6- and 2,7-bis(MM)N isomers in the reaction mixtures.

As stated in Section **3.3.1,** in the optimised reaction of dimethoxymethane and naphthalene over Hβ, naphthalene (10 mmol) was stirred with DMM (758 mmol) with Hβ (Si/Al 12.5, 4 g) for 4 h at 120 °C), bis(MM)N was observed in an 18 % yield as a mixture of three isomers. Using the original GC peak areas for calculation purposes, rather than the rounded yield figures for the individual isomers, the ratio of the 2,6-:2,7-bis(MM)N isomers was seen to be 5.8.

Also recorded in Section **3.3.1**, the optimised reaction of dimethoxymethane and naphthalene over HM, (naphthalene (10 mmol) was stirred with DMM (758 mmol) with HM (Si/Al 40, 8 g) for 4 h at 120 °C), gave a mixture of 2,6- and 2,7-bis(MM)N isomers in a 45 % yield. In this case the 2,6/2,7 ratio was 17.0, based on the original GC peak areas.

Therefore, the reaction of dimethoxymethane and naphthalene was more selective towards the favoured 2,6-bis(MM)N isomer when HM was employed, compared to when Hβ was employed. HM was also found to be more selective towards 2-MMN in the initial methoxymethylation of naphthalene, and a higher 2/1 ratios was observed with HM compared to Hβ (2/1 ratio of 3.2 and 2.2 observed, respectively). Furthermore, the yield of bis(MM)N isomers was also higher with HM as the catalyst.

3.3.8 Summary and Conclusions

In this section of work the separation of individual bis(MM)N isomers from crude reaction mixtures was attempted by column chromatography and reduced pressure distillation. Three bis(MM)N isomers were observed in the optimised reaction of dimethoxymethane and naphthalene with Hβ (retention times 39.4 min, 44.1 min and 44.3 min by GC analysis), and two bis(MM)N isomers were observed in the optimised reaction of dimethoxymethane and naphthalene with HM (retention times 44.1 min and 44.3 min by GC analysis).

The major isomer in the reactions with HM and Hβ had a retention time of 44.3 min. This isomer was isolated (white crystals) from the crude mixture by a combination of column chromatography and Kugelröhr distillation, and characterised by NMR.

The separation of bis(MM)N isomers with retention times 39.4 min and 44.1 min was unsuccessful. However, the isomers were characterised by NMR analysis of mixtures of isomers. Reported below is a summary of the findings.

- The major bis(MM)N isomer (retention time **44.3 min**) observed in the reaction of dimethoxymethane and naphthalene over Hβ and HM, corresponded to the desired **2,6-bis(MM)N** isomer.
- The isomer with retention time **44.1 min** observed in the reaction of dimethoxymethane and naphthalene over Hβ and HM, corresponded to **2,7-bis(MM)N**.
- The isomer with retention time **39.4 min** observed in the reaction of dimethoxymethane and naphthalene over Hβ, corresponded to **2,3-bis(MM)N**.

- → A **2,6/2,7 ratio** of **5.8** was observed in the optimised reaction of dimethoxymethane and naphthalene over **Hβ**.
- → A **2,6/2,7** ratio of **17.0** was observed in the optimised reaction of dimethoxymethane and naphthalene over **HM**.

In conclusion, the reaction of dimethoxymethane and naphthalene was reasonably selective towards the desired 2,6-bis(MM)N isomer when HM was employed, with a 2,6/2,7 ratio of 17.0 being observed.

In view of this, it was decided to carry out the methoxymethylation of 2-MMN over HM, in an attempt to improve the yield of bis(MM)N with an increased selectivity towards to 2,6-bis(MM)N. This will be discussed in greater detail in Chapter 4.

3.3.9 Spectral properties of the bis(MM)N isomers

The ^{1}H NMR and ^{13}C NMR details recorded below were obtained from the following spectra:

(a) spectra of 2,6-bis(MM)N were recorded on a pure sample obtained following chromatography and Kugelröhr distillation;

(b) details of 2,7-bis(MM)N were deduced from spectra of a mixture of 2,6- and 2,7-bis(MM)N isomers (ratio ca. 17:1), by subtracting the known spectra of the 2,6-isomer;

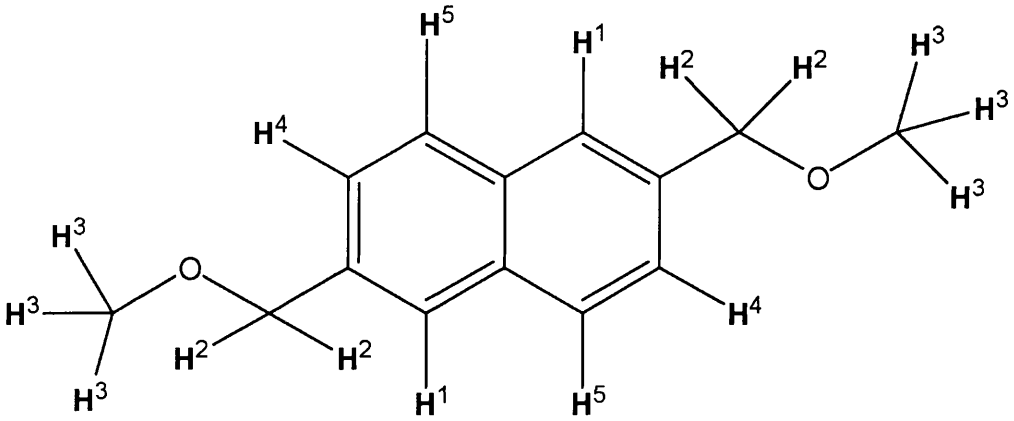
(c) details of 2,3-bis(MM)N were deduced from spectra of a mixture of 2,3-, 2,6- and 2,7- isomers (ca. 4:2:14 ratio). Mass Spectra were obtained from a GC/MS run on the mixture of isomers.

3.3.10 Analytical data

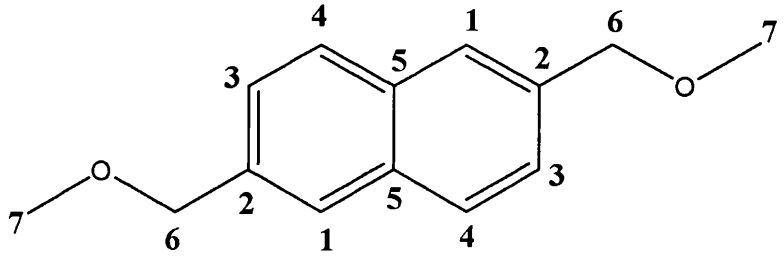
2,6-bis(methoxymethyl)naphthalene

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent

(Assignments confirmed by 2D ^{1}H - ^{13}C correlation)



$\delta^{1}H$: 7.76 (2H, d, J = 8 Hz, H^5), 7.71 (2H, s, H^1), 7.47 (2H, d, J = 8 Hz, H^4), 4.54 (4H, s, H^2), 3.58 (6H, s, H^3)



$\delta^{13}C$: 136.1 (C^2), 133.2 (C^5), 129.0 (C^4), 127.4 (C^3), 126.8 (C^1), 75.0 (C^6), 58.5 (C^7).

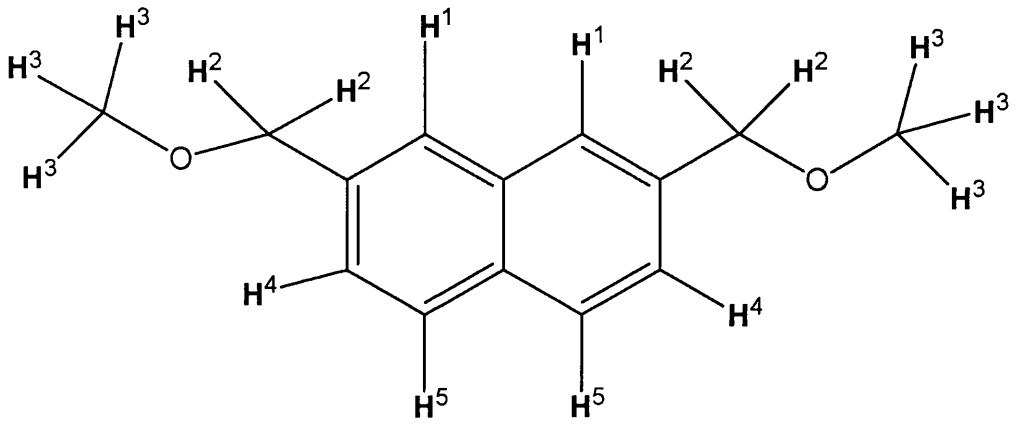
MS: (from GCMS)

EI m/z (% abundance): 216 (41) [M^+], 184 (79), 169 (81), 141 (100), 115 (66).

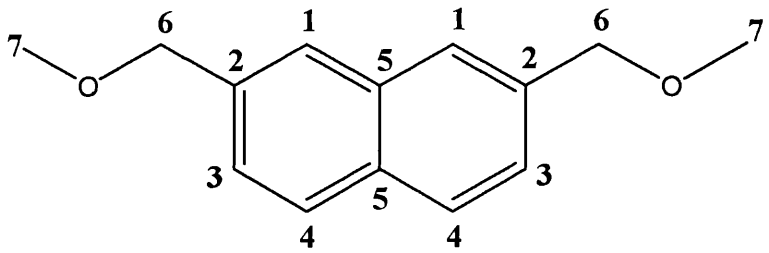
2,7-bis(methoxymethyl)naphthalene

(From mixed NMR analysis with 2,6- bis(MM)N)

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



δ^{1}H: 7.75 (2H, d, J =8 Hz, H^5), 7.70 (2H, s, H^1), ca. 7.45 (2H, d, J = 8 Hz, H^4), 4.55 (4H, s, H^2), 3.55 (6H, s, H^3).



δ^{13}C: 136.2 (C^2), 133.3 (C^5), 129.0 (C^4), 127.1 (C^3), 126.9 (C^1), 75.2 (C^6), 58.6 (C^7).

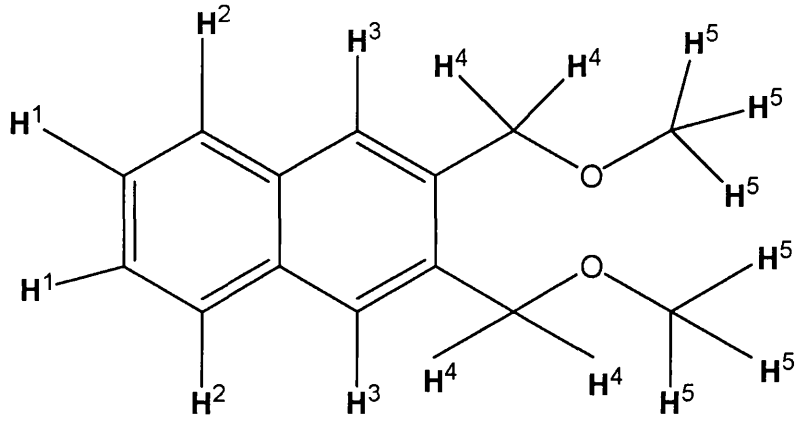
MS: (from GCMS)

EI m/z (% abundance): 216 (100) [M^+], 185 (96), 155 (71), 141 (89), 115 (53).

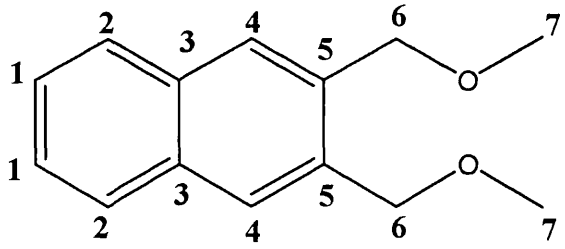
2,3-bis(methoxymethyl)naphthalene

(Deduced from NMR analysis of its mixture with 2,6- bis(MM)N and 2,7-bis(MM)N)

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



$\delta^{1}H$: δ 7.77 (2H, m, H^2), δ 7.72 (2H, s, H^3), δ 7.45 (2H, m, H^1), δ 4.55 (4H, s, H^4), δ 3.55 (6H, s, H^5).



$\delta^{13}C$: 135.5 (C^5), 133.3 (C^3), 129.3 (C^4), 127.1 (C^2), 126.9 (C^1), 75.2 (C^6), 58.6 (C^7).

MS: (from GCMS)

EI m/z (% abundance): 216 (93) [M^+], 185 (89), 171 (75), 141 (100), 115 (61).

Chapter 4

Methoxymethylation of 2-MMN

4.1 Introduction

It was shown in Chapter 3 that MMN and bis(MM)N are generated in a reasonable yield in the zeolite catalysed reaction of naphthalene and dimethoxymethane under relatively mild conditions (120 °C, 4 h). The highest conversion of naphthalene (90 %) was achieved when HM (Si/Al 40) was employed in the reaction. A 45 % yield of MMN and a 45 % yield of bis(MM)N were observed, respectively under optimised conditions (4 h, 120 °C) when 10 mmol of naphthalene was reacted with 758 mmol of DMM in the presence of HM (8 g).

Even though a good yield of MMN and bis(MM)N were observed when HM (Si/Al 40) was employed, the reaction was not very selective towards the favoured 2-MMN isomer, with a 2/1 ratio of 3.0 being observed. The reaction was more selective in the second substitution, and two bis(MM)N isomers were observed out of a possible ten (45 % yield of bis(MM)N was observed, desired 2,6-bis(MM)N was the major isomer with a 42 % yield being observed, minor isomer observed in a 3 % yield).

It was decided to carry out the direct methoxymethylation of 2-MMN in an attempt to increase the yield of bis(MM)N. This reaction is essentially mimicking the second substitution in the methoxymethylation of naphthalene and would therefore give a good insight into what to expect, if the selectively of the initial methoxymethylation of naphthalene was improved, to give 2-MMN as the major isomer.

4.2 Initial results of the methoxymethylation of 2-MMN

4.2.1 Effect of Hβ and HM

An initial set of experiments was carried out with 2-(methoxymethyl)naphthalene and dimethoxymethane catalysed by zeolites; HM (Si/Al 40) and Hβ (Si/Al 12.5) (HM and Hβ chosen on the basis of the results observed in reactions with naphthalene and dimethoxymethane in Chapter 3). Both reactions were carried out under identical conditions in a stirred mini reactor at 120 °C for 4 h, under self generated pressure. 2-(Methoxymethyl)naphthalene (10 mmol) was reacted with dimethoxymethane (758 mmol) and catalyst (4 g), following the procedure outlined in **Section 3.1.11** in Part 1 of Chapter 3. The results are reported in Table 4.1.

4.2.2 Synthesis of 2-(methoxymethyl)naphthalene via a known route

Difficulties were encountered when isolating 2-MMN from the reaction mixture (separation of 2-MMN by column chromatography and reduced pressure distillation were attempted several times with no success) owing to the similar physical properties of 1-MMN and 2-MMN. Therefore, a pure sample of 2-MMN was synthesised via a known route from 2-naphthalenemethanol, iodomethane and *tert*-butyllithium (as described in **Section 3.1.11** in Part 1 of Chapter 3).

4.2.3 Presentation of results

The mol % recovery of 2-(methoxymethyl)naphthalene, mol % yield of bis(methoxymethyl)naphthalene (3 isomers detected), 2,6/2,7 ratio and total mol % are presented.

The proportions of recovered 2-(methoxymethyl)naphthalene and products formed were determined from calculations based on GC analysis. Numbers are

expressed as percentages and have been rounded to the nearest whole number, except numbers that are < 1 which are expressed to 1 decimal place.

The 2,6/2,7 ratio corresponds to the ratio of the 2,6- and 2,7- isomers of bis(methoxymethyl)naphthalene. This ratio was determined by a direct comparison of GC peak areas, not rounded numbers.

Table 4.1: Effect of Hβ and HM on the reaction between 2-(methoxymethyl)naphthalene and dimethoxymethane[a]

Zeolite	Hbeta (12.5)	HM (40)
Swansea experiment code	di-MMN-1	di-MMN-HM
MMN recovery (%)	45	37
Bis(MM)N (%)	52	57
2,6/2,7 ratio	8.6	9.7
Total (%)	97	94

[a] 4 h stirred mini reactor reaction at 120 °C under self generated pressure; 2-MMN (1.72 g, 10 mmol), dimethoxymethane (57.6g, 758 mmol) catalyst (4 g, Hβ, Si/Al 12.5) and (4g, HM, Si/Al 45).

The reaction occurred to a greater extent when HM was employed, compared to the reaction that employed Hβ, and a 63 % and 55 % conversion of 2-MMN was observed, respectively. A 57 % yield of bis(MM)N was observed with HM, comprising two isomers by GCMS analysis, (the major isomer was the desired 2,6-bis(MM)N). The yield of bis(MM)N was lower when Hβ was employed; a 52 % yield of bis(MM)N was observed comprising three isomers by GCMS analysis.

In addition, the reaction was more selective towards the favoured 2,6-bis(MM)N isomer when HM was employed, compared to the reaction with Hβ. A 2,6/2,7 ratio of

9.7 was observed with HM, compared to a 2,6/2,7 ratio of 8.6 observed with Hβ. The recovery of material from the reaction mixture was lower in the reaction with HM, compared to the recovery observed in the reaction with Hβ (94 % and 97 %, respectively).

4.2.4 Comparing the methoxymethylation of 2-MMN and naphthalene over HM and Hβ

In general, a higher conversion was observed in the methoxymethylation of naphthalene (82 % conversion observed with Hβ, 90 % conversion observed with HM under optimised conditions), compared to the methoxymethylation of 2-MMN (55 % conversion with Hβ, 63 % conversion with HM).

In the methoxymethylation of both naphthalene and 2-MMN it was found that the reaction occurred to a greater extent with HM, compared to Hβ.

A significant increase in the yield of bis(MM)N was observed in the methoxymethylation of 2-MMN, compared to the methoxymethylation of naphthalene over both Hβ and HM. An 18 % yield of bis(MM)N was observed in the methoxymethylation of naphthalene over Hβ, compared to a 52 % yield of bis(MM)N in the methoxymethylation of 2-MMN over Hβ. A 45 % yield of bis(MM)N was observed in the methoxymethylation of naphthalene over HM, compared to 57 % yield of bis(MM)N in the methoxymethylation of 2-MMN over HM.

With regards to the selectivity of the methoxymethylation of naphthalene compared to the methoxymethylation of 2-MMN, the same trends were observed. Three isomers of bis(MM)N were observed in the methoxymethylation of both naphthalene and 2-MMN over Hβ, whereas two isomers of bis(MM)N were observed in the methoxymethylation of naphthalene and 2-MMN over HM (desired 2,6-bis(MM)N major isomer).

The 2,6/2,7 ratio was higher in the methoxymethylation of 2-MMN compared to the methoxymethylation of naphthalene when Hβ was employed, with a 2,6/2,7 ratio of 8.6 and 5.8 being observed, respectively. Conversely, the 2,6/2,7 ratio was significantly lower in the methoxymethylation of 2-MMN compared to the methoxymethyaltion of naphthalene when HM was employed, with a 2,6/2,7 ratio of 9.7 and 16.8 being observed, respectively. Although a decrease in selectivity was observed, the reactions that employed HM were largely more selective than the reactions that employed Hβ.

The most significant difference in the methoxymethylation of 2-MMN compared to the methoxymethylation of naphthalene over Hβ, was the dramatic improvement in the recovery of material from the reaction mixture. 97 % of material was recovered from the reaction mixture in the reaction with 2-MMN catalysed by Hβ, where as a 74 % recovery of material from the reaction mixture was observed in the reaction with naphthalene, catalysed by Hβ. This suggests that less coke was formed in the methoxymethylation of 2-MMN compared to the methoxymethylation naphthalene over Hβ.

In summary, a higher yield of bis(MM)N was observed (regarding reactions with both HM and Hβ) in the methoxymethylation of 2-MMN, compared to the methoxymethylation of naphthalene. In addition, a higher selectivity was observed when HM was employed (methoxymethylation of naphthalene and 2-MMN), compared to the reactions which employed Hβ.

In conclusion, the methoxymethylation of 2-MMN over HM showed great potential in terms of selectively producing high yields of 2,6-bis(MM)N. Therefore, this reaction was investigated further.

4.3 Yield optimisation of bis(methoxymethyl)naphthalene) with HM

4.3.1 Investigating different reaction parameters

A series of optimisation reactions were carried out with HM in which several reaction parameters were varied, in attempt to increase the conversion and selectivity towards the favoured 2,6-bis(MM)N isomer. These included reactions designed to investigate the effects of reaction time, reaction temperature and the amount of HM added to the reaction. The results are discussed in the following sections.

The first study involved the effect of reaction time to determine if 4 h was the optimal length of reaction. The reaction time was varied from 4 h to 48 h and the results are reported in Table 4.2.

4.4 Increasing reaction time with HM

As the length of reaction was increased from 4 h to 48 h, the conversion of 2-MMN also increased. A 63 % conversion of 2-MMN was observed when the reaction was carried out for 4 h, and an 89 % conversion was observed when the reaction time was increased to 24 h. The conversion increased even further when the reaction was carried out for 48 h, and a 93 % conversion was observed.

Even though the conversion of 2-MMN increased on increasing the reaction time, the yield of bis(MM)N decreased. A 57 % yield of bis(MM)N was observed when the reaction was carried out for 4 h, which decreased to 53 % when the reaction was carried out for 24 h. The yield of bis(MM)N decreased even further when the reaction time was increased to 48 h, and a 40 % yield of bis(MM)N was observed.

In addition to the decreased yield of bis(MM)N, the selectivity of the reaction also decreased on increasing the reaction time. A 2,6/2,7 ratio of 9.7 was observed when the reaction was carried out for 4 h, compared to a 2,6/2,7 ratio of 6.7 being observed when the length of reaction was increased to 24 h. A further decrease in

selectivity was observed when the reaction was carried out for 48 h, with a 2,6/2,7 ratio of 5.6 being observed.

The recovery of material from the reaction mixture steadily decreased as the length of the reaction was increased from 4 h to 48 h. When the reaction was carried out for 4 h, 94 % of material was recovered from the reaction mixture. When the reaction time was increased to 24 h, the recovery of material from the reaction mixture decreased to 64 %. A further decrease in material recovery was observed when the length of reaction was increased to 48 h, where only 47 % of material was recovered from the reaction mixture.

Table 4.2: Increasing the reaction time in the reaction of 2-(methoxymethyl)naphthalene and dimethoxymethane over HM[a]

Time	4 h	24 h	48 h
Swansea experiment code	di-MMN-HM	di-MMN-HM-24	di-MMN-HM-48
MMN recovery (%)	37	11	7
Bis(MM)N (%)	57	53	40
2,6/2,7 ratio	9.7	6.7	5.6
Total (%)	94	64	47

[a] Stirred mini reactor reaction at 120 °C under self generated pressure for various lengths of time; 2-MMN (1.72 g, 10 mmol), dimethoxymethane (57.6g, 758 mmol) catalyst (4g, HM, Si/Al 40).

These results suggest that as the reaction time was increased from 4 h to 48 h, bis(MM)N may have reacted further with DMM or another molecule of 2-MMN to produce polysubstituted naphthalene rings or polyaromatic compounds (coke). These products may have got trapped within the internal channels of HM. This offers a reasonable explanation as to why the increased conversion of 2-MMN was not coupled with an increase in the yield of bis(MM)N. The formation of coke would also

account for the decrease in the recovery of material from the reaction mixture as the length of reaction was increased.

In conclusion, there was no benefit to the reaction in terms of the yield of bis(MM)N or selectivity towards the desired 2,6-isomer, when the reaction time was increased past 4 h. Therefore, further reactions were carried out at 4 h.

4.5 Increasing the reaction temperature with HM

In order to establish the optimal temperature for the methoxymethylation of 2-MMN, a series of experiments was carried out where the temperature was varied from 120 °C to 160 °C, in 20 °C stages, following the procedure outlined in **Section 3.1.11** in Part 1 of Chapter 3. The results are reported in Table 4.3.

When the reaction temperature was increased from 120 °C to 140 °C the conversion of 2-MMN increased from 63 % to 87 %, respectively. When the reaction temperature was increased further to 160 °C the conversion decreased slightly, with an 83 % conversion being observed.

Table 4.3: Increasing the reaction temperature in the reaction of 2-(methoxymethyl)naphthalene and dimethoxymethane over HM[a]

Temp	120 °C	140 °C	160°C
Swansea experiment code	di-MMN-HM	di-MMN-HM-140	di-MMN-HM-160
MMN recovery (%)	37	13	17
Bis(MM)N (%)	57	63	22
2,6/2,7 ratio	9.7	6.4	3.0
Total (%)	94	76	39

[a] 4 h stirred mini reactor reaction at under self generated pressure at various temperatures; 2-MMN (1.72 g, 10 mmol), dimethoxymethane (57.6g, 758 mmol) catalyst (4g, HM, Si/Al 40).

The yield of bis(MM)N increased from 57 % when the reaction was carried out at 120 °C, to 63 % when the reaction was carried out at 140 °C. Conversely, the yield of bis(MM)N significantly decreased when the reaction temperature was increased further to 160 °C, with a 22 % yield being observed.

The selectivity of the reaction decreased as the reaction temperature was increased from 120 °C to 140 °C, with a 2,6/2,7 ratio of 9.7 and 6.4 being observed, respectively. When the reaction temperature was increased to 160 °C, the selectivity decreased even further with a 2,6/2,7 ratio of 3.0 being observed.

The recovery of material from the reaction mixture also decreased as the reaction temperature was increased. 94 % of material was recovered from the reaction mixture when the reaction was carried out at 120 °C, compared to 76 % of material recovered from the reaction mixture when the reaction was carried out at 140 °C.

When the reaction temperature was increased further to 160 °C, the recovery of material from the reaction mixture decreased to just 39 %.

The results suggested that coke formation was encouraged when the reaction temperature was increased beyond 120 °C. This would explain why the conversion of 2-MMN increased on increasing the reaction temperature from 120 °C to 160 °C, while the yield of bis(MM)N and the recovery of material from the reaction mixture both decreased.

One can conclude that there was no improvement to the yield of bis(MM)N or enhanced selectivity towards 2,6-bis(MM)N when the reaction temperature was increased from 120 °C to 160 °C. In light of this information, further reactions were carried out at 120 °C.

4.6 Increasing the amount of catalyst

It was decided to investigate the effect of HM on the yield and selectivity of the desired product. In order to determine the optimal amount of HM for the methoxymethylation of 2-MMN, a series of experiments was carried out where the amount of HM was varied from 4 g to10 g, following the procedure outlined in **Section 3.1.11** in Part 1 of Chapter 3. The results are reported in Table 4.4.

The conversion increased when the amount of HM added to the reaction mixture was increased from 4 g to 8, with a 63 % and 68 % conversion being observed, respectively. The reaction occurred to a lesser extent when the reaction was carried out in the presence of 10 g of HM, and the conversion decreased to 49 %.

The yield of bis(MM)N decreased on increasing the amount of catalyst, a 57 % yield of bis(MM)N being observed when 4 g of HM was employed, compared to a 55 % yield of bis(MM)N observed when 8 g of HM was employed. The yield of

bis(MM)N decreased even further when 10 g of HM was employed, with a 48 % yield was observed with 10 g of HM.

The selectivity of the reaction increased as the amount of HM added to the reaction mixture was increased. A 2,6/2,7 ratio of 9.7 was observed when 4 g of HM was employed, compared to a 2,6/2.7 ratio of 10.5 observed when 8 g of HM was employed. The selectivity increased even further when 10 g of HM was employed, with a 2,6/2,7 ratio of 10.8 being observed.

Table 4.4: Increasing the amount of HM zeolite catalyst in the reaction of 2-(methoxymethyl)naphthalene and dimethoxymethane[a]

Catalyst	4 g	8 g	10 g
Swansea experiment code	di-MMN-HM	di-MMN-HM-8	di-MMN-HM-10
MMN recovery (%)	37	32	22
Bis(MM)N (%)	57	55	48
2,6/2,7 ratio	9.7	10.5	10.8
Total (%)	94	87	70

[a] 4 h stirred mini reactor reaction at 120 °C under self generated pressure; 2-MMN (1.72 g, 10 mmol), dimethoxymethane (57.6g, 758 mmol) catalyst (HM, Si/Al 40).

The recovery of material from the reaction mixture decreased as the amount of HM added to the reaction was increased from 4 g to 10 g. 94 % of material was recovered from the reaction mixture when 4 g of HM was employed, which decreased to 87 % when 8 g of HM was employed. This decreased even further when 10 g of HM was employed, with only 70 % of the material being recovered from the reaction mixture.

The decrease in the recovery of material from the reaction mixture can be attributed to the increase in conversion observed when the amount of HM was increased, coupled with a decrease in the yield of bis(MM)N (probably due to an increase in coke formation in the presence of more catalyst).

4.7 General Discussion

1. In order to achieve a reasonable conversion of 2-MMN, certain minimum conditions of time, temperature, and amount of HM (Si/Al 40), are required.

2. Forcing conditions (elevated temperatures, long reaction times and large amounts of catalyst) lead to reductions in bis(MM)N, although other reactions are able to continue (probably further reaction of bis(MM)N with DMM or 2-MMN), leading to the production of material that cannot be extracted from the zeolite (coke), resulting in a poor recovery of material from the reaction mixture.

3. HM was more selective than Hβ in the methoxymethylation of 2-MMN. In the reaction with HM two bis(MM)N isomers were observed, and 2,6-bis(MM)N was the major isomer. In the reaction with Hβ, three bis(MM)N isomers were observed.

4.8 Summary and conclusions

In the initial methoxymethylation of 2-MMN, HM was more active than Hβ with a higher conversion being observed. HM was also found to be more selective than Hβ, and a higher 2,6/2,7 ratio was observed. In addition to this, only two bis(MM)N isomers were observed with HM (2,6-bis(MM)N being the major isomer), compared to three bis(MM)N isomers observed with Hβ.

Therefore, the reaction with HM was chosen for further optimisation in an attempt to increase the yield of bis(MM)N, and the selectivity towards the favoured 2,6- isomer. Reactions were carried out under forcing conditions (increased time and temp) and with more catalyst. The general trends are reported below.

Increasing reaction time:

Increasing the reaction time resulted in increased conversion, decreased bis(MM)N yield, decreased 2,6/2,7 ratio, and decreased recovery of material from the reaction mixture.

Increasing reaction temp:

Increasing the reaction temperature resulted in increased conversion and increased bis(MM)N yield up to a point (120 °C and 140 °C respectively), and then a decrease, along with decreased selectivity and decreased recovery of material from the reaction mixture.

Increasing the amount of catalyst:

Increasing the amount of catalyst resulted in increased conversion, decreased yield of bis(MM)N and decreased selectivity. In addition, the amount of material recovered from the reaction mixture also decreased.

It was found that the reaction was limited under forcing reaction conditions and the yield of products and the recovery of material both decreased at elevated

temperatures, extended reactions times and in the presence of large amounts of catalyst. This was thought to be due to secondary reactions (of bis(MM)N with DMM or 2-MMN), that generated compounds that lead to the coking of the zeolite. This trend was also observed in the methoxymethylation of naphthalene over Hβ.

The best result so far in the methoxymethylation of 2-MMN over HM, was a 57 % yield of bis(MM)N (2,6-bis(MM)N major isomer) with a 2,6/2,7 ratio of 9.7, with a 94 % recovery of material from the reaction mixture. This was achieved with 2-MMN (10 mmol), DMM (758 mmol) and HM (4 g) under relatively mild reaction conditions (4 h at 120 ° C).

4.9 Experimental

The reaction procedure was identical to that set out in Section **3.1.11** in Part 1 of Chapter 3, with the exception of different substrate, where reactions were carried out with 2-MMN instead of naphthalene. GC analysis was identical to that described in Section **3.1.12** in Part 1 of Chapter 3.

Chapter 5, Part 1

Yield optimisation of EMN

5.1.1 Introduction

In Chapter 3 the methoxymethylation of naphthalene was investigated extensively. A high conversion of naphthalene (90 %) was observed under optimised conditions (120 ° C, 4 h) over Zeolite HM, to give a high yield of the desired products (45 % MMN and 45 % bis(MM)N). The reaction was not very selective towards the favoured 2-MMN isomer in the initial methoxymethylation of naphthalene, with a 2/1 ratio of 3.0 being observed. Conversely, the reaction was more selective in the second methoxymethylation of naphthalene and 2,6-bis(MM)N was the major isomer.

The low selectivity in the initial methoxymethylation of naphthalene would be limiting in the commercial production of 2,6-bis(MM)N (and ultimately PEN), because 2-MMN and 1-MMN are extremely difficult to separate due to their similar physical properties. In view of this it was decided to investigate the ethoxymethylation of naphthalene (where diethoxymethane is the alkoxyalkylating agent), to determine if a higher selectivity towards the 2-EMN isomer could be achieved.

The ethoxymethylation of naphthalene was briefly investigated in Part 1 of Chapter 3 (reported in **Table 3.1.2**), the most encouraging reaction being over Zeolite HM (150 ° C, 18 h), with a 33 % yield of EMN and 2/1 ratio of 1.9 being observed. Therefore, the reaction between diethoxymethane and naphthalene over Zeolite HM was investigated further.

5.1.2 Yield optimisation of (ethoxymethyl)naphthalene over HM

5.1.2.1 Investigating different reaction parameters

A series of optimisation reactions was carried out in which several reaction parameters were varied, in an attempt to increase both the yield of and selectivity for the desired product. These included reactions designed to probe the effects of increasing the Si/Al ratio of HM, reaction temperature, length of reaction, amount of catalyst, and volume of alkoxyalkylating agent. The results are shown in the following sections. The first study involved increasing the Si/Al ratio of HM.

5.1.2.2 Presentation of results

The mol % recovery of naphthalene, mol % yield of ethylnaphthalene (2 isomers detected), mol % yield of (ethoxymethyl)naphthalene (EMN, 2 isomers detected), 2/1 ratio of the EMN isomers, and total mol % (i.e. the sum of the yields of the identified products) are presented.

The proportions of recovered naphthalene and products formed were determined from calculations based on GC analysis. Numbers are expressed as percentages and have been rounded to the nearest whole number, except numbers that are < 1 which are expressed to 1 decimal place.

The 2/1 ratio corresponds to the ratio of the 1 and 2 isomers of (ethoxymethyl)naphthalene. This ratio was determined by a direct comparison of GC peak areas.

5.1.3 Increasing the Si/Al ratio of HM

It was shown in the methoxymethylation of naphthalene that increasing the Si/Al ratio of HM brought about an increased conversion and selectivity (**Table 3.2.10,** Part 2 of Chapter 3). In an attempt to increase the yield of EMN and the selectivity towards the favoured 2-isomer, a reaction was carried out with HM (Si/Al

ratio 40) and compared to the reaction with HM (Si/Al ratio 10). The reaction was carried out under optimised conditions established for the methoxymethylation of naphthalene (120 °C, 4 h self generated pressure). Naphthalene (10 mmol) was reacted with DEM (535 mmol) and HM (Si/Al ratio 40, 4 g), using the procedure set out in Section **3.1.11** in Part 1 of Chapter 3. The results are reported in Table 5.1.1.

It should be noted that the reaction with HM (Si/Al ratio 10) was carried out under different conditions (150 °C, 18 h, self generated pressure), which were employed in the initial alkoxyalkylation experiments reported in Part 1 of Chapter 3, where naphthalene (10 mmol) was reacted with DEM (80 mmol) in the presence of cyclohexane (60 ml) and HM (Si/Al ratio 10, 4 g).

On increasing the Si/Al ratio of HM from 10 to 40, the conversion of naphthalene decreased. A 47 % conversion was observed in the reaction with HM Si/Al 10, compared to a 13 % conversion observed in the reaction with HM Si/Al 40. Product formation decreased on increasing the Si/Al ratio of HM. Ethylnaphthalene was observed in an 8 % yield when HM Si/Al 10 was employed and it was not observed in the reaction that employed HM Si/Al 40. In addition, the yield of EMN decreased; a 33 % yield of EMN was observed in the reaction with HM Si/Al 10, which decreased to 10 % in the reaction with HM Si/Al 40.

Table 5.1.1 : Increasing the Si/Al ratio of HM zeolite catalyst in the reaction of naphthalene and diethoxymethane

Si/ Al ratio of HM	10[x]	40[y]
Swansea experiment code	D8a	DEM67
Naphthalene recovery (%)	53	87
Ethylnaphthalene (%)	8	0
EMN (%)	33	10
2/1 ratio	1.9	13.0
Total (%)	94	97

[x] 18 h stirred mini reactor reactions at 150 °C under self generated pressure; catalyst (4 g HM Si/Al 10), naphthalene (1.28 g, 10 mmol), diethoxymethane (8.32 g, 80 mmol) and cyclohexane as solvent (60 ml).
[y] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g HM Si/Al 40), naphthalene (1.28 g, 10 mmol), diethoxymethane (55.64 g, 535mmol).

The selectivity of the reaction increased significantly when the Si/Al ratio of HM was increased from 10 to 40. A 2/1 ratio of 1.9 was observed in the reaction with HM Si/Al 10, compared to a 2/1 ratio of 13.0 being observed in the reaction with HM Si/Al 40. The recovery of material from the reaction mixture also increased on increasing the Si/Al of HM, with 94 % and 97 % of material being recovered when HM Si/Al 10 and HM Si/Al 40 were used, respectively.

Due to the dramatic increase in selectivity when the Si/Al ratio was increased, further reactions were carried out with HM (Si/Al ratio 40).

5.1.4 Varying the volume of diethoxymethane with HM

In an attempt to determine the effect of the volume of reagent on the conversion and selectivity of the reaction, a series of experiments was carried out where the

volume of diethoxymethane was varied from 160 mmol to 535 mmol. The reactions were carried out using the same procedure outlined in Section **3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.1.2.

Table 5.1.2: Effect of varying the volume of diethoxymethane in the reaction of naphthalene and diethoxymethane catalysed by HM[a]

DEM (mmol)	160	320	400	535
Swansea experiment code	DEM-20	DEM-40	DEM-50	DEM-67
Naphthalene recovery (%)	82	90	91	87
Ethylnaphthalene (%)	0	0	0	0
EMN (%)	15	9*	9	10
2/1 ratio	7.9	10.1	10.9	13.0
Total (%)	97	99	100	97

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; naphthalene (1.28 g, 10 mmol), diethoxymethane (varying amounts), catalyst (4 g HM, Si/Al 40).
* Mixture of (methoxymethyl)naphthalene and (ethoxymethyl)naphthalene

The conversion of naphthalene decreased on increasing the volume of diethoxymethane from 160 mmol to 400 mmol. An 18 % conversion, 10 % conversion and 9 % conversion were observed when 160 mmol, 320 mmol and 400 mmol of diethoxymethane were employed, respectively. In the reaction where 535 mmol of diethoxymethane was employed, the naphthalene conversion increased slightly to 13 %.

The yield of EMN decreased when the volume of diethoxymethane was increased from 160 mmol to 320 mmol, and a 15 % yield and 9 % yield of EMN were observed, respectively. When the volume of reagent was increased further to 400

mmol and 535 mmol, a 9 % yield and a 10 % yield of EMN were observed, respectively. Ethylnaphthalene was not observed in any of the reactions.

The selectivity of the reaction steadily increased as the volume of diethoxymethane was increased from 160 mmol to 535 mmol. A 2/1 ratio of 7.9 was observed when the reaction was carried out with 160 mmol of diethoxymethane, with a 2/1 ratio of 10.1 being observed in the reaction with 320 mmol. The 2/1 ratio increased even further when 400 mmol and 535 mmol of diethoxymethane were employed, with a 2/1 ratio of 10.0 and 13.0 being observed, respectively.

The recovery of material from the reaction mixture increased slightly when the volume of diethoxymethane was increased from 160 mmol to 400 mmol (97 % and 100 % recovery of material, respectively). The recovery of material from the reaction mixture then decreased to 97 %, when the reaction was carried out with 535 mmol of diethoxymethane.

Further reactions were carried out with 535 mmol of diethoxymethane, because the reaction was the most selective in the presence of this volume of reagent.

5.1.5 Varying the reaction time

A series of experiments was carried out where the reaction time was varied from 1 h to 72 h, in an attempt to increase the conversion of naphthalene to EMN. The reactions were conducted using the same procedure outlined in Section **3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.1.3.

Table 5.1.3: Effect of varying the reaction time in the reaction of naphthalene and diethoxymethane catalysed by HM[a]

Time (h)	1	2	4	8	72
Swansea experiment code	HM(40)1	HM(40)2	HM(40)4	HM(40)8	HM(40)72
Naphthalene recovery (%)	92	88	87	82	80
Ethylnaphthalene (%)	0	0	0	0	0
EMN (%)	5	10	10	10	8
2/1 ratio	12.0	12.2	13.0	11.0	11.0
Total (%)	97	98	97	92	88

[a] Stirred mini reactor reactions at 120 °C under self generated pressure with varying reaction times; catalyst (4 g, HM, Si/Al: 40), naphthalene (1.28 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol).

As the length of reaction was increased from 1 h to 72 h, the conversion of naphthalene also increased. When the reaction was carried out for 1 h an 8 % conversion of naphthalene was observed, this increased to 12 % and 13 % when the reaction was carried out for 2 h and 4 h, respectively. The conversion increased even further when the length of reaction was increased to 8 h, and an 18 % conversion was observed. When the reaction time was increased to 72 h, the conversion increased to 20 %.

The yield of EMN increased as the reaction time was increased from 1 h to 8 h. A 5 % yield of EMN was observed when the reaction was carried out for 1 h, which increased to 10 % when the reaction time was increased to 2 h. When the reaction was carried out for 4 h and 8 h, the yield of EMN did not increase any further and a 10 % yield of EMN was observed in both reactions. A decrease in the yield of EMN (8 %) was observed when the reaction time was extended to 72 h.

The selectivity of the reaction increased as the reaction time was increased from 1 h to 4 h. A 2/1 ratio of 12.0 was observed when the reaction was carried out for 1h, which increased to 12.2 when the reaction time was increased to 2 h. A further increase in selectivity was observed when the reaction was carried out for 4 h, with a 2/1 ratio of 13.0 being observed. When the reaction time exceeded 4 h the selectivity decreased, with a 2/1 ratio of 11.0 being observed when the reaction was carried out for 8 h or 72 h.

The recovery of material from the reaction mixture decreased as the length of reaction was increased from 1 h to 72 h. When the reaction was carried out for 1 h, 97 % of material was recovered from the reaction mixture. When the reaction time was increased to 2 h and 4 h, the recovery of material decreased to 98 % and 97 %, respectively. A further decrease in material recovery was observed when the length of reaction was increased further, with a 92 % recovery being observed after 8 h of reaction time and 88 % recovery being observed after 72 h of reaction time.

This suggests EMN may have reacted to give compounds with high molecular weight as the reaction time was increased. For example, EMN could have reacted with DEM to give polysubstituted naphthalene products or with a further molecule of EMN to give a bridged product. These compounds may be too large to exit the zeolite framework, which would offer a reasonable explanation to why product recovery decreases on increasing the reaction time.

In view of this, it appears that the optimal reaction time in terms of naphthalene conversion and yield of EMN was 4 h. Therefore, further reactions were continued at 4 h.

5.1.6 Varying the reaction temperature

In an attempt to determine the optimal reaction temperature, to give a maximum yield of EMN and good selectivity towards the favoured 2-EMN isomer, a series of reactions was carried out where the reaction temperature was varied from 60 °C to 160 °C in 20 °C stages. The reactions were carried out using the same procedure outlined in Section **3.1.13.1** in Part 1 of Chapter 3, and the results are reported in Table 5.1.4

Table 5.1.4: Effect of varying the reaction temperature in the reaction of naphthalene and diethoxymethane catalysed by HM[a]

Temp (°C)	60	80	100	120	140	160
Swansea experiment code	HM(40)60	HM(40)80	HM(40)100	HM(40)120	HM(40)140	HM(40)160
Naphthalene recovery (%)	90	90	87	87	86	86
Ethylnaphthalene (%)	0	0	0	0	0	0
EMN (%)	7	8	8	10	11	11
2/1 ratio	0.56	0.78	11.6	13.0	11.0	9.4
Total (%)	97	98	95	97	97	97

[a] 4 h stirred mini reactor reactions under self generated pressure at various temperatures; catalyst (4 g HM, Si/Al 40), diethoxymethane (55.64 g, 535 mmol); naphthalene (1.28 g, 10 mmol).

On increasing the reaction temperature from 60 °C to 160 °C, the conversion of naphthalene also increased. When the reaction was carried out at 60 °C and 80 °C a 10 % conversion was observed, which increased to 13 % when the reaction temperature was increased to 100 °C. A 13 % conversion was also observed when the reaction was carried out at 120 °C. When the reaction was carried out at 140 °C, the

conversion increased to 14 %, but no further increase in conversion was observed when the reaction temperature was increased further to 160 °C.

The yield of EMN also increased on increasing the reaction temperature. A 7 % yield of EMN was observed when the reaction was carried out at 60 °C, this increased to 8 % when the reaction temperature was increased to 80 °C. No further increase in EMN yield was observed when the reaction was carried out at 100 °C. On increasing the reaction temperature to 120 °C a 10 % yield of EMN was observed, which increased to 11 % when the reaction temperature was increased to 140 °C and 160 °C.

The selectivity of the reaction significantly increased when the reaction temperature was increased from 60 °C to 120 °C. A 2/1 ratio of 0.56 was observed when the reaction was carried out at 60 °C, compared to a 2/1 ratio of 0.78 when the reaction was carried out at 80 °C. A dramatic increase in selectivity was observed when the reaction was carried out at 100 °C, with a 2/1 ratio of 11.6 being observed. The selectivity increased even further when the reaction temperature was increased to 120 °C, with a 2/1 ratio of 13.0 being observed. On increasing the reaction temperature to 140 °C and 160 °C the selectivity decreased, with a 2/1 ratio of 11.0 and 9.4 being observed, respectively.

The dramatic increase in selectivity observed when the reaction temperature was increased from 60 °C to 120 °C could be rationalised in terms of thermodynamic control. There are two possible isomers of (ethoxymethyl)naphthalene; 1-EMN which is referred to as the kinetic product (the isomer which is formed fastest) and 2-EMN which is referred to as the thermodynamic product (the most thermodynamically stable isomer) (Section 3.1.4 in Part 1 of Chapter 3). The amount of each isomer

formed during a reaction can be determined by the reaction conditions, for example by varying the reaction temperature. When a reaction is carried out at low temperature it is said to be under kinetic control. Thus, the major product would have been the kinetically favoured 1-EMN. This could explain the low 2/1 ratio observed when the reaction was carried out under 120 °C.

Similarly, when the reaction temperature was increased further than 120 °C an increase in the 2/1 ratio was observed. The reaction may have been under thermodynamic control, therefore an increase in the formation of the thermodynamically stable 2-EMN would occur. This would lead to an increased 2/1 ratio being observed as the reaction temperature was increased.

The recovery of material was largely unaffected by the increase in the reaction temperature, with between 95 % and 97 % of material being recovered from the reaction mixture, in each of the reactions carried out between 60 °C and 160 °C.

In conclusion, the optimal reaction temperature was 120 °C where a reasonable yield of EMN and selectivity were achieved. Therefore, further reactions were carried out at 120 °C.

5.1.7 Varying the amount of HM Zeolite catalyst

In an attempt to push the reaction further and increase the conversion of naphthalene and the yield of EMN, reactions were carried out where the amount of HM was varied from 2 g to 15 g. The reactions were carried out using the same procedure outlined in Section **3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.1.5.

The results reported in Table 5.1.5 illustrate how the conversion increased as the amount of HM was increased from 2 g to 15 g. A 9 % conversion was observed when the reaction was carried out with 2 g of HM, which increased to 13 % when the

amount of HM was increased to 4 g. When 6 g of HM was employed in the reaction the conversion of naphthalene increased to 14 %, which increased to 20 % when 8 g of HM was employed. A more significant increase in conversion was observed when 10 g and 15 g of HM were employed, with a 28 % and 32 % conversion being observed, respectively.

In general, the yield of EMN increased as the amount of HM added to the reaction mixture was increased. A 5 % yield of EMN was observed when 2 g of HM was employed, which increased to 10 % when the amount of HM was increased to 4 g. A further 2 % increase was observed in the reaction with 6 g of HM (12 % yield). On increasing the amount of HM to 8 g and 10 g, 17 % and 19 % yields of EMN were observed, respectively. The yield of EMN decreased to 15 % when the amount of HM employed was 15 g.

Table 5.1.5: Effect of increasing the amount of HM zeolite in the reaction of naphthalene and excess diethoxymethane[a]

Amount of Cat	2	4	6	8	10	15
Swansea experiment code	DEM- 2g	DEM- 4g	DEM- 6g	DEM- 8g	DEM-10g	DEM-15g
Naphthalene recovery (%)	91	87	86	80	72	68
Ethylnaphthalene (%)	0	0	0	0	0	0
EMN (%)	5	10	12	17	19	15
2/1 ratio	15.7	13.0	10.6	9.7	9.9	7.6
Total (%)	96	97	98	97	91	83

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (HM Si/Al 40, varying amounts), diethoxymethane (55.64 g, 535 mmol); naphthalene (1.28 g, 10 mmol)

The selectivity of the reaction decreased as the amount of HM added to the reaction was increased from 2 g to 8 g. A 2/1 ratio of 15.7 was observed in the reaction that employed 2 g of HM, compared to a 2/1 ratio of 13.0 observed in the reaction that employed 4 g of HM. A further decrease in selectivity was observed when the amount of HM was increased to 6 g and 8 g, with 2/1 ratios of 10.6 and 9.7 being observed, respectively. When the reaction was carried out with 10 g of HM, the selectivity increased slightly, with a 2/1 ratio of 9.9 being observed. The selectivity then decreased when the amount of HM employed was 15 g, with a 2/1 ratio of 7.6 being observed.

The recovery of material from the reaction mixture was largely unchanged when the amount of HM was varied between 2 g and 8 g, and between 96 % and 98 % of material was recovered. When the reaction was carried out with 10 g of HM, the recovery of material decreased slightly to 91 %, a further decrease in the recovery of material being observed (83 %) when 15 g of HM was employed.

The increase in conversion observed with 15 g of HM was coupled with a decrease in the yield of EMN, leading to a decrease in the recovery of material from the reaction mixture. This was probably due to further reaction of EMN with another molecule of EMN to form a bridged compound which may have got stuck within the pores of the zeolite.

It was clear that the conversion of naphthalene increased and the reaction occurred to a greater extent when more HM was added to the reaction mixture. Although, one would have expected a more significant increase in the yield of EMN than was observed, as both naphthalene and diethoxymethane were still present in the reaction mixture after 4 h.

5.1.8 Influence of ethanol on the rate of reaction.

In the methoxymethylation of naphthalene (over Hβ) discussed in Section 2 of Chapter 3, it was found that the presence of methanol in the reaction mixture generated during the reaction from dimethoxymethane, served to decrease the rate of the reaction resulting in a decreased conversion and yield of products. The relationship was proportional, and the naphthalene conversion decreased as the volume of methanol added to the reaction mixture increased (**Table 3.2.2**). It was thought this was due to the interaction of methanol with the zeolitic protons. This may have reduced the catalytic activity of the zeolite thus decreasing conversion.

It was shown by GC analysis that ethanol was generated during the course of the reaction between diethoxymethane and naphthalene over HM. In view of this, it was decided to investigate the influence of ethanol on the rate of the reaction between diethoxymethane and naphthalene.

5.1.8.1 Addition of ethanol to the reaction mixture

A series of reactions was carried out between naphthalene (10 mmol), diethoxymethane (535 mmol) and HM (4 g), in which the amount of ethanol added to the reaction mixture was nothing or varied from 0.5 ml to 10 ml. Reactions were carried out for 4 h at 120 °C using the procedure outlined in Section **3.1.11**, in Section 1 of Chapter 3. The results are reported in Table 5.1.6. (The total amount of ethanol in the reaction mixture included the ethanol generated during the course of the reaction, in addition to the ethanol added at the start of the reaction).

An 11 % conversion of naphthalene was observed in the reaction where ethanol was not added to the reaction mixture at the start of the reaction. The conversion decreased when 0.5 ml and 1 ml of ethanol was added to the reaction mixture with a 9 % conversion being observed in both of the reactions. When the

amount of ethanol added to the reaction mixture was increased to 5 ml and 10 ml, the conversion increased and an 11 % conversion was observed in each of the reactions.

Table 5.1.6: The effect of adding ethanol to the reaction of naphthalene and diethoxymethane catalysed by HM[a]

Ethanol (ml)	0	0.5	1	5	10
Swansea experiment code	DEM60-EtOH-0	DEM60-EtOH-0.5	DEM60-EtOH-1	DEM60-EtOH-5	DEM60-EtOH-10
Naphthalene recovery (%)	89	91	91	89	89
Ethylnaphthalene (%)	0	0	0	0	0
EMN (%)	10	9	9	10	10
2/1 ratio	13.8	14.1	13.0	6.9	5.5
Total (%)	99	100	100	99	99

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (4 g HM, Si/Al 40), naphthalene (1.28 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol), ethanol (varying amounts).

The yield of EMN followed the same trend, a 10 % yield of EMN being observed in the reaction when ethanol was not added to the reaction mixture at the start of the reaction. When the amount of ethanol added to the reaction mixture was 0.5 ml or 1 ml, the yield of EMN decreased, with a 9 % yield of EMN being observed in each of the reactions. When the amount of ethanol added to the reaction mixture was increased to 5 ml and 10 ml, the yield of EMN increased, with a 10 % yield of EMN being observed in each reaction.

The selectivity of the reaction steadily decreased as the amount of ethanol added to the reaction mixture was increased from 0.5 ml to 10 ml. A 2/1 ratio of 13.8 was observed in the reaction when ethanol was not added to the reaction mixture, at the start of the reaction. The 2/1 ratio changed to 14.1 and 13.0, when the amount of ethanol added to the reaction mixture was 0.5 ml and 1 ml, respectively. A further decrease in selectivity was observed when the amount of ethanol added to the reaction

mixture was increased to 5 ml and 10 ml, with a 2/1 ratio of 6.9 and 5.5 being observed, respectively.

One can conclude that the addition of ethanol to the reaction mixture did not slow down the reaction significantly, and the conversion of naphthalene and yield of EMN were largely unaffected. The selectivity towards the favoured 2-EMN isomer decreased as the amount of ethanol added to the reaction mixture was increased.

Therefore, the presence of ethanol in the reaction mixture did not have a limiting effect on the rate of reaction. The fact that the reaction between diethoxymethane and naphthalene did not reach completion, even under forcing conditions, was more likely due to the physical restraints of the reaction (e.g. bulky diethoxymethane reagent). This will be discussed in more detail in the next section.

5.1.9 Comparing the ethoxymethylation and methoxymethylation of naphthalene over HM

There were several notable differences between the reaction of diethoxymethane with naphthalene, and the reaction of dimethoxymethane with naphthalene over HM (Si/Al 40).

The first major difference between the two reactions was the extent to which the reaction took place. It was found that a smaller amount of catalyst was required in the reaction with dimethoxymethane to give a larger conversion of naphthalene, compared to the reaction with diethoxymethane under the same conditions (120 °C, 4 h).

A 90 % conversion of naphthalene was achieved in the reaction between dimethoxymethane and naphthalene when the amount of HM (Si/Al 40) employed was 4 g, compared to a 28 % conversion of naphthalene observed in the reaction between diethoxymethane and naphthalene in the presence of 10 g of HM (Si/Al 40).

The ethoxymethylation and methoxymethylation of naphthalene reaction conditions were identical except for the different reagents (diethoxymethane and dimethoxymethane, respectively). This suggested that the reason why the ethoxymethylation of naphthalene occurred to a lesser extent than the methoxymethylation of naphthalene was due to the reagents themselves and their interaction with naphthalene and the zeolite.

Diethoxymethane is a bulkier reagent than dimethoxymethane, therefore the rate of diffusion of DEM into the pores of HM may have been slower than the rate of diffusion of DMM into the pores of HM. Consequently, a slower rate of reaction and a lower conversion of naphthalene would be observed in the ethoxymethylation of naphthalene compared to the methoxymethylation of naphthalene.

In addition, bis(EM)N was not observed in the reaction between diethoxymethane and naphthalene, whereas bis(MM)N was observed in a 45 % yield in the optimised reaction between dimethoxymethane and naphthalene. This could also be explained in terms of the bulky diethoxymethane reagent.

The reaction between diethoxymethane and naphthalene was far more selective than the reaction between dimethoxymethane and naphthalene, when catalysed by HM (Si/Al 40) under the same conditions. A 2/1 ratio of 9.9 was observed in the optimised reaction with diethoxymethane with 10 g of HM (17 % yield of EMN). The reaction was even more selective with 2 g of HM with a 2/1 ratio of 15.7 being observed, although the reaction occurred to a lesser extent and a lower yield of EMN was observed (5 %).

The high selectivity observed with DEM can be explained in terms of the shape selectivity of the catalyst (discussed in Chapter 1). One would predict that 1-EMN is less linear than 2-EMN, therefore the channels within the HM framework

may have facilitated the β substitution of naphthalene rather than the α substitution of naphthalene. Thus, a greater amount of 2-EMN than 1-EMN would be observed.

The reaction between dimethoxymethane and naphthalene was less selective, with a 2/1 ratio of 3.0 being observed in the optimised reaction (a higher selectivity was observed in the second substitution where 2,6-bis(MM)N was the major isomer).

The low selectivity observed with DMM can be explained in similar terms; 1-MMN is less linear than 2-MMN therefore a higher proportion of 2-MMN was observed compared to 1-MMN. But the 2/1 ratio of MMN was much lower than the 2/1 ratio of EMN. This is probably because MMN is a smaller molecule than EMN, therefore the formation of 1-EMN would have been more restricted by the size constraints of the Zeolite than the formation of 1-MMN. In other words the Zeolite was more shape selective towards the 2-EMN isomer in the ethoxymethylation of naphthalene, compared to the 2-MMN isomer in the methoxymethylation of naphthalene.

In summary, both the ethoxymethylation and methoxymethylation of naphthalene have their relative advantages and disadvantages as a route for producing an intermediate in the synthesis of PEN. The ethoxymethylation of naphthalene would be a superior method if the high selectivity achieved was coupled with an increased conversion of naphthalene, to give high yields of EMN and bis(EM)N. On the other hand, the methoxymethylation of naphthalene would be a superior method if the selectivity of the initial substitution could be increased, or if a method could be developed in order to achieve a good separation of the 1-MMN and 2-MMN isomers.

5.1.10 Attempts to increase the selectivity towards the favoured 2-EMN

Several avenues for increasing the conversion of the reaction had been explored. Therefore, attention was focused on increasing the selectivity of the reaction towards the favoured 2-EMN isomer.

5.1.10.1 Application of dealuminated HM (Si/Al: 40)

It was shown in Part 2 of Chapter 3 that an increase in selectivity was observed when dealuminated HM was employed. Therefore, it was decided to employ dealuminated HM (**Sample A**, 4 M HCL for 24 h) in the reaction of DEM with naphthalene under optimised conditions (4 h, 120 °C). Naphthalene (10 mmol) and diethoxymethane (535 mmol) were stirred with dealuminated HM (Si/Al 40, 10 g) and compared to the reaction that employed the same quantity of non-dealuminated HM (Si/Al ratio 40). The reaction was carried out using the same procedure as set out in Section **3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.1.7.

A decrease in conversion was observed in the reaction with dealuminated HM (Si/Al ratio 40) compared to the reaction with non-dealuminated HM (Si/Al ratio 40), with a 9 % and 28 % conversion being observed, respectively. The yield of EMN also decreased in the reaction with dealuminated HM, with a 7 % yield of EMN being observed in the reaction with dealuminated HM, compared to a 19 % yield being observed with non-dealuminated HM.

Table 5.1.7: Application of dealuminated HM (Si/Al 40) to the reaction of naphthalene and diethoxymethane under optimised conditions (4 h, 120 °C under self generated pressure [a]

Zeolite	HM (40)	HM (Sample A)
Swansea experiment code	EMN-10g	EMN-10gdealumA
Naphthalene recovery (%)	72	91
Ethylnaphthalene (%)	0	0
EMN (%)	19	7
2/1 ratio	9.9	2-only
Total (%)	91	98

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; HM (10 g,), naphthalene (1.28 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol).

The decrease in conversion and product yield can be attributed to a decrease in the number of active sites in the dealuminated HM due to a significant proportion of aluminium being removed, compared to the non-dealuminated HM. Even though stronger acid sites are present, if significant aluminium is removed the observed effect would be reduced activity due to significantly fewer sites. These results suggest that there is an optimum Si/Al ratio for HM, in order to achieve maximum conversion of naphthalene into EMN.

The selectivity of the reaction significantly improved when dealuminated HM was employed, compared to the selectivity observed in the reaction that employed non-dealuminated HM. It was found that only 2-EMN was observed in the presence of dealuminated HM.

If one could increase the conversion of naphthalene to give a higher yield of 2-EMN, this reaction would be very promising and be a great starting block in the production of 2,6-bis(EM)N.

5.1.11 Summary and conclusions

The reaction between naphthalene and diethoxymethane catalysed by Zeolite HM was chosen for optimisation, based on the results obtained from an initial study of the reaction in Part 1 of Chapter 3, in an attempt to selectively produce high yields of 2,6-bis(EM)N.

It was found that the reaction between diethoxymethane and naphthalene did not reach completion under forcing conditions. This was thought to be due to the slow diffusion of the bulky diethoxymethane reagent into Zeolite HM resulting in a slow rate of reaction. Furthermore, the yield of EMN and the recovery of material both decreased when too much force was used. This was thought to be due to secondary reactions which produced compounds that were non-retractable from the HM catalyst. The general trends are reported below.

Increasing the Si/Al ratio of HM:

Increasing the Si/Al ratio of HM resulted in a decreased conversion and decreased yields of ethylnaphthalene and (ethoxymethyl)naphthalene, while the 2/1 ratio significantly increased.

Increasing the volume of diethoxymethane:

Increasing the amount of diethoxymethane from 160 mmol to 400 mmol resulted in decreased conversion and a decreased yield of EMN. Increasing the volume to 535 mmol increased the conversion and yield of EMN. The 2/1 ratio increased steadily.

Increasing the reaction time:

Increasing the reaction time resulted in increased conversion. The yield of EMN increased to a point (8 h) then decreased and the 2/1 ratio increased to a point (4 h) then decreased.

Increasing the reaction temp:

Increasing the reaction temperature resulted in an increased conversion and increased yield of EMN. The 2/1 ratio increased to a point (120 °C) then decreased.

Increasing the amount of catalyst:

Increasing the amount of catalyst resulted in an increased conversion, increased yield of EMN and decreased 2/1 ratio.

Addition of ethanol to the reaction mixture:

The addition of ethanol to the reaction mixture resulted in a decrease in selectivity, but conversion and product yield were largely unaffected.

Application of dealuminated HM (Si/Al 40):

Dealuminated HM (40) resulted in a decreased conversion, decreased yield of EMN and increased selectivity (only 2-EMN was observed).

When comparing the ethoxymethylation and methoxymethylation of naphthalene, one can conclude that a lower conversion of naphthalene was observed in the ethoxymethylation of naphthalene, although the reaction was more selective and a higher 2/1 ratio was observed.

The best result so far was a 19 % EMN yield with a 2/1 ratio of 9.9. This was achieved with naphthalene (10 mmol), DEM (535 mmol) and HM (Si/Al 40,10 g) under relatively mild reaction conditions (4 h at 120 ° C).

The ethoxymethyaltion of 2-EMN is investigated in Chapter 6, in an attempt to produce 2,6-bis(EM)N selectively for use in the production of PEN.

5.1.12 Experimental

The reaction procedure was identical to that set out in Section **3.1.11** in Part 1 of Chapter 3. Any exceptions are described in the footnotes under the relevant results table. GC analysis was identical to that described in Section **3.1.12** in Part 2 of Chapter 3.

5.1.12.1 Dealumination of the HM catalyst by acid leaching

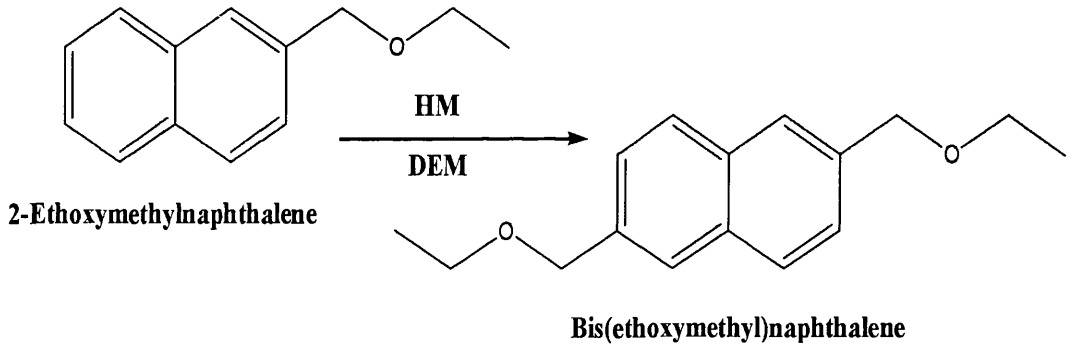
Dealuminated Sample A was obtained using the procedure set out in Section **3.2.19.1** in Part 2 of Chapter 3.

Chapter 5, Part 2

Ethoxymethylation of 2-EMN

5.2.1 Introduction

In Part 1 of this Chapter, the reaction between diethoxymethane (DEM) and naphthalene over HM was investigated extensively. EMN isomers were observed in a reasonable yield (19 %) from the reaction of naphthalene (10 mmol), DEM (535 mmol) and HM (Si/Al 40, 10 g), under relatively mild reaction conditions (4 h at 120 ° C), but bis(EM)N was not observed. Therefore, it was decided to carry out a reaction between 2-(ethoxymethyl)naphthalene (2-EMN) and diethoxymethane over HM (**Reaction scheme 5.2.1**), in an attempt to produce 2,6-bis(EM)N selectively.



Reaction scheme 5.2.1: Reaction of 2-(ethoxymethyl)naphthalene and diethoxymethane catalysed by HM zeolite.

5.2.2 Synthesis of 2-(ethoxymethyl)naphthalene via an authentic route

Difficulties were encountered when isolating pure 2-EMN from the reaction mixture (separation of 2-EMN by column chromatography and reduced pressure distillation were attempted several times with no success), owing to the similar physical properties of 1-EMN and 2-EMN. Therefore, a pure sample of 2-EMN was synthesised via a known route from 2-naphthalenmethanol, iodoethane and *tert*-butyllithium (as described in Section **5.2.14.1**) and used in the following reactions.

5.2.3 Initial results of the ethoxymethylation of 2-EMN over HM

An initial reaction was carried out with 2-(ethoxymethyl)naphthalene (10 mmol), diethoxymethane (535 mmol) and HM (Si/Al 40, 4 g) under mild conditions (4 h, 120 ° C, self generated pressure). The reaction was carried out using the same procedure as outlined in **Section 3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.2.1.

The mol % recovery of 2-(ethoxymethyl)naphthalene, mol % yield of bis(ethoxymethyl)naphthalene (1 isomer detected), and total mol % are presented. The proportions of recovered 2-(ethoxymethyl)naphthalene and products formed were determined from calculations based on GC analyses. Numbers are expressed as percentages and have been rounded to the nearest whole number, except numbers that are < 1 which are expressed to 1 decimal place.

Table 5.2.1: Table to show the results of the initial ethoxymethylation of 2-(ethoxymethyl)naphthalene over HM zeolite[a]

	Initial Reaction
Swansea experiment code	di-EMN-1
EMN recovery (%)	97
Bis(EM)N (%)	3
Total (%)	100

[a] 4 h stirred mini reactor reaction at 120 °C under self generated pressure; 2-EMN (1.86 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol), catalyst (4 g HM, Si/Al 40).

As shown in Table 5.2.1, the reaction occurred to a small extent, with a 3 % conversion of 2-EMN being observed. GC analysis of the reaction mixture gave a peak at 46.72 min, which corresponded to a compound with a Mr of 244 by GCMS analysis. This suggested that a single isomer of bis(EM)N was produced (3 % yield).

5.2.4 Yield optimisation of bis(EM)N

5.2.4.1 Investigating different reaction parameters

In an attempt to increase the conversion of 2-EMN and give a higher yield of bis(EM)N, a series of optimisation reactions was carried out. Several reaction parameters were varied, including: reaction temperature, length of reaction, amount of catalyst, and different zeolites. The results are shown in the following sections. The first study involved increasing the reaction temperature.

5.2.4.2 Effect of reaction temperature

To determine the optimal temperature for the ethoxymethylation of 2-EMN, a series of reactions was carried out where the reaction temperature was varied from 120 °C to 180 °C. The reactions were carried out using the same procedure as outlined in Section **3.1.11** in Part 1 of Chapter 3. GC analysis showed that some of the reaction mixtures contained several by-products, and the first task was therefore to identify these compounds.

5.2.4.3 Formation of by products

When the reaction temperature was increased above 120 °C, GC analysis of the reaction mixtures showed that several by products were observed. Compounds with retention times of 35.86 min, 36.14 min and 40.32 min were observed in addition to 2-EMN (retention time 38.20 min) and bis(EM)N (retention time 46.72 min).

The compounds with retention times 35.86 min and 36.14 min each had a relative molecular mass of 172 according to GCMS analysis; corresponding to 1- and 2-(methoxymethyl)naphthalene, respectively (confirmed by co-injections of pure samples of 1- and 2-MMN with the reaction mixture).

The compound with retention time 40.32 min had a relative molecular mass of 200 according to GCMS analysis, thought to be ethyl(methoxymethyl)naphthalene,

abbreviated to **Et(MMN)**. A pure sample of Et(MMN) was not available for co-injection and attempts to isolate the compound were unsuccessful, therefore it was impossible to carry out a full characterisation.

The mechanism for the production of MMN and Et(MMN) was not clear. It is conceivable that a reverse reaction took place to give naphthalene, which could react further with a methoxymethyl group to give 1- and 2-MMN (The source of methoxymethyl groups was not obvious, but it may have been present as an impurity in diethoxymethane). Furthermore, ethylation of MMN (source of ethyl groups from ethanol, generated from diethoxymethane) would generate Et(MMN).

5.2.4.4 Estimation of response factor for Et(MMN)

As previously mentioned, attempts to isolate Et(MMN) by column chromatography and distillation were unsuccessful. Without a pure sample of Et(MMN) an accurate response factor could not be calculated, and used to determine the percentage yield of Et(MMN) in the reaction mixture. An approximate response factor was estimated, based on the response factors of the other products which were calculated using pure samples.

1- and 2-MMN had retentions times of 35.86 min and 36.14 min, respectively, each with a response factor of 0.72. 2-EMN had a retention time of 38.2 min, with a response factor of 0.63. Bis(EM)N had a retention time of 46.72 min, with a response factor of 0.22. Et(MMN) had a retention time of 40.32 min, therefore it was estimated that the response factor for Et(MMN) would be approximately 0.55. Using these response factors, yields for the various products could be calculated and are reported in Table 5.2.2.

Table 5.2.2: The effect of increasing the reaction temperature in the reaction of 2-(ethoxymethyl)naphthalene and diethoxymethane over HM[a]

Temp (°C)	120	140	160	170	180
Swansea experiment code	di-EMN120	di-EMN140	di-EMN160	di-EMN170	di-EMN180
EMN recovery (%)	99	94	80	66	65
MMN (%)	0	0	3	2	4
Et(MMN) (%)	0	0	1	5	5
Bis(EM)N (%)	1	4	16	26	26
Total (%)	100	98	100	99	100

[a] 4 h stirred mini reactor reaction at various temperatures under self generated pressure; catalyst (4 g HM, Si/Al 40), 2-EMN (1.86 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol).

An increase in conversion was observed on increasing the reaction temperature from 120 °C to 180 °C. A 1 % conversion of 2-EMN was observed when the reaction was carried out at 120 °C, which increased to 6 % and 20 % when the reaction temperature was increased to 140 °C and 160 °C, respectively. When the reaction temperature was increased to 170 °C and 180 °C, a further increase in the conversion of 2-EMN was observed (34 % and 35 %, respectively).

MMN was not observed when the reaction was carried out at 120 °C and 140 °C. When the reaction temperature was increased to 160 °C, MMN was observed in a 3 % yield, and this yield remained more or less constant when the reaction temperature was increased further.

In line with this, Et(MMN) was also not observed when the reaction was carried out at 120 °C and 140 °C. When the reaction was carried out at 160 °C,

Et(MMN) was observed in a 1 % yield, which increased to 5 % when the reaction temperature was increased to 170 °C or 180 °C.

The yield of bis(EM)N also increased on increasing the reaction temperature from 120 °C to 180 °C. When the reaction was carried out at 120 °C a 1 % yield of bis(EM)N was observed, which increased to 4 % and 16 % when the reaction was carried out at 140 °C and 160 °C, respectively. A further increase in the yield of bis(EM)N was observed when the reaction temperature was increased to 170 °C, with a 26 % yield being observed. When the reaction temperature was increased to 180 °C, no further increase in product yield was observed (26 % yield).

Further reactions were carried out at 170 °C, since an optimum yield of bis(EM)N (26 %) was achieved at this reaction temperature.

5.2.5 Increasing the reaction time

In an attempt to determine if the yield of bis(EM)N would increase when the reaction time was increased, a reaction was carried out where the length of reaction was increased to 24 h and compared to the reaction that was carried out for 4 h. The same reaction procedure was used as described in Section **3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.2.3.

The investigation into the effect of reaction time was limited to two reactions, since it was shown in the ethoxymethylation of naphthalene that an increase in the length of reaction had little effect on the product yield (Table 5.1.3 in Part 1 of this Chapter). In addition, the recovery of material from the reaction mixture had decreased when the reaction time was increased to 72 h.

An increase in conversion was observed when the reaction time was increased from 4 h to 24 h. A 34 % conversion of 2-EMN was observed when the reaction was

carried out for 4 h, compared to a 42 % conversion of 2-EMN being observed when the reaction time was increased to 24 h.

An increase in the yield of MMN was also observed when the reaction time was increased from 4 h to 24 h. A 2 % yield of MMN was observed when the reaction was carried out for 4 h, compared to a 19 % yield being observed when the reaction was carried out for 24 h.

One can speculate that increasing the reaction time may have lead to the degradation of (ethoxymethyl)naphthalene to (methoxymethyl)naphthalene. Thus a higher conversion of (ethoxymethyl)naphthalene coupled with an increased yield of (methoxymethyl)naphthalene would be observed.

The yield of Et(MMN) did not increase when the reaction time was increased, with a 5 % yield being observed when the reaction was carried out for 4 h or 24 h. The yield of bis(EM)N decreased when the reaction time was increased. A 26 % yield of bis(EM)N was observed when the reaction was carried out for 4 h, with an 18 % yield being observed when the reaction time was increased to 24 h.

Table 5.2.3: Effect of increasing the reaction time in the reaction of 2-(ethoxymethyl)naphthalene and diethoxymethane over HM[a]

Time (h)	4	24
Swansea experiment code	di-EMN170	di-EMN170-24
EMN recovery (%)	66	58
MMN (%)	2	19
Et(MMN) (%)	5	5
Bis(EM)N (%)	26	18
Total (%)	99	100

[a] Stirred mini reactor reaction at 170 °C under self generated pressure for various lengths of time; catalyst (4 g HM, Si/Al 40), 2-EMN (1.86 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol).

There was no added benefit to the reaction in terms of increased yield of bis(EM)N when the reaction time was increased from 4 h to 24 h. Therefore, further reactions were carried out at 4 h.

5.2.6 Increasing the amount HM

In an attempt to push the reaction further and increase the conversion of 2-EMN, a series of reactions was carried out where the amount of HM was increased from 4 g to 12 g in 2 g stages. The reactions were carried out using the same procedure as outlined in Section **3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.2.4.

Table 5.2.4: Effect of increasing the amount of HM catalyst in the reaction of 2-(ethoxymethyl)naphthalene and diethoxymethane[a]

Amnt Cat	4 g	6 g	8 g	10 g	12 g
Swansea experiment code	di-EMN4g	di-EMN6g	di-EMN8g	di-EMN10g	di-EMN12g
EMN recovery (%)	66	72	74	41	40
MMN (%)	2	0	0	0	0
Et(MMN) (%)	5	6	4	10	10
Bis(EM)N (%)	26	22	21	25	22
Total (%)	99	100	100	76	72

[a] 4 h stirred mini reactor reaction at 170 °C under self generated pressure; catalyst (HM, Si/Al 40, varying amounts), 2-EMN (1.86 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol).

A decrease in conversion was observed when the amount of HM added to the reaction was increased from 4 g to 8 g. A 34 % conversion of 2-EMN was observed when the reaction was carried out with 4 g of HM, but the conversion decreased to 28 % when the amount of catalyst was increased to 6 g. A further decrease in conversion

was observed when the amount of catalyst was increased to 8 g, with a 26 % conversion being observed. When the amount of catalyst was increased to 10 g, the conversion significantly increased, with a 59 % conversion of 2-EMN being observed. The conversion increased even further to 60 %, when the amount of HM was increased to 12 g. However, in these latter two cases, the total recovery of material was significantly reduced, so it is possible that the increased conversion is not real, but that the reduced recovery when a large amount of zeolite is used merely gives an appearance of greater conversion.

A 2 % yield of MMN was observed when the reaction was carried out with 4 g of HM, but when the amount of HM exceeded 4 g MMN was not observed. By contrast, the yield of Et(MMN) increased marginally as the amount of catalyst added to the reaction mixture was increased from 4 g to 6 g. A 5 % yield of Et(MMN) was observed when 4 g of HM was employed, compared to a 6 % yield when 6 g of HM was employed. The yield of Et(MMN) was about the same when 8 g of HM was employed, but a further increase in the yield of Et(MMN) was observed when the amount of HM was increased to 10 g and 12 g, with a 10 % yield of Et(MMN) being observed in both reactions.

The yield of bis(EM)N was largely unaffected when the amount of HM added to the reaction was increased from 4 g to 12 g, with between 21 % and 26 % yield of bis(EM)N being observed in all of the reactions.

The increased conversion of 2-EMN observed when the amount of HM was increased from 4 g to 12 g was not coupled with an increased yield of bis(EM)N. Therefore, the recovery of material from the reaction mixture decreased as the amount of HM added to the reaction mixture was increased. When the reaction was carried out in the presence of 4 g, 6 g and 8 g of HM, nearly all the material was recovered

from the reaction mixture. When the reaction was carried out in the presence of 10 g of HM, the recovery of material from the reaction mixture decreased to 76 %. A further decrease in material recovery was observed when the amount of HM added to the reaction mixture was increased to 12 g, with 72 % of material being recovered from the reaction mixture.

A feasible explanation could be that in the presence of large amounts of catalyst, further reactions of 2-EMN with DEM, or with a further molecule of 2-EMN could be encouraged to give compounds of high molecular weight (coke), which could get stuck within the channels of HM, resulting in a low recovery of material. However, it is also possible that it is simply more difficult to extract all of the material from large amounts of zeolite and that more washes were needed.

One can conclude that an increase in bis(EM)N was not observed when the amount of catalyst added to the reaction mixture was increased. The optimal yield of bis(EM)N, coupled with a good recovery of material from the reaction mixture was achieved in the reaction that employed 4 g of HM.

5.2.7 Application of Hβ to the optimised reaction between diethoxymethane and 2-ethoxymethylnaphthalene

In an attempt to determine if an increase in the conversion of 2-EMN would be observed in the presence of a different zeolite, it was decided to carry out a reaction between diethoxymethane and 2-(ethoxymethyl)naphthalene catalysed by Hβ.

2-EMN (10 mmol) and DEM (535 mmol) were stirred with Hβ (4 g) under optimised conditions (4 h, 120 °C), and compared to the analogous reaction catalysed by HM. The reaction was carried out using the same procedure as described in Section **3.1.11** in Part 1 of Chapter 3, and the results are reported in Table 5.2.5.

Table 5.2.5: Application of Hβ zeolite in the reaction of 2-(ethoxymethyl)naphthalene and diethoxymethane under optimised conditions[a]

Zeolite	HM	HB
Swansea experiment code	Di-EMN170	DiEMNHB170
2-EMN recovery (%)	66	79
MMN (%)	2	12
Et(MMN)(%)	5	0
Bis(EM)N (%)	26	3
Total (%)	99	94

[a] 4 h stirred mini reactor reactions at 170 °C under self generated pressure; catalyst (4 g), 2-EMN (1.86 g, 10 mmol), diethoxymethane (55.64 g, 535 mmol).

A decrease in conversion was observed when Hβ was employed, compared to the reaction that employed HM, with 21 % conversion and 34 % conversion being observed, respectively. A 2 % yield of MMN was observed in the reaction with HM, but 12 % when Hβ was employed, under the same conditions. Conversely, the yield of Et(MMN) decreased when Hβ was employed. Et(MMN) was observed in a 5 % yield in the reaction with HM, but it was not observed at all in the reaction with Hβ.

The yield of bis(EM)N was significantly lower when Hβ was employed in the reaction between diethoxymethane and naphthalene than in the analogous reaction with HM. A 26 % yield and 3 % yield were observed, respectively. In addition, a decrease in the recovery of material was observed when Hβ was employed. In the reaction with HM, 99 % of material was recovered from the reaction mixture

compared to 94 % of material being recovered from the reaction mixture in the reaction with Hβ.

In conclusion, the reaction between diethoxymethane and 2-(ethoxymethyl)naphthalene occurred to a lesser extent and gave a lower yield of bis(EM)N when Hβ was employed, compared to the reaction in which HM was employed.

5.2.8 Varying the alkoxyalkylating agent with HM under optimised conditions

Reactions carried out in the previous sections between diethoxymethane and 2-EMN over HM illustrated that low conversions of 2-EMN and low yields of bis(EM)N were observed (34 % conversion of 2-EMN and 26 % yield of bis(EM)N in the optimised reaction), even under forcing conditions (elevated temperatures and increased amounts of catalyst). This was thought to be due to the slow diffusion of diethoxymethane and/or 2-EMN into the pores of HM (size constraints of HM), resulting in a slow rate of reaction and low conversions of 2-EMN. (This phenomenon was also observed in the reactions with diethoxymethane and naphthalene over HM, reported in Part 1 of this Chapter).

In the analogous reactions of dimethoxymethane with naphthalene and 2-MMN over HM (reported in Chapter 3 and Chapter 4, respectively), higher conversions of naphthalene and 2-MMN and higher yields of bis(MM)N were observed (63 % conversion in the case of 2-MMN, 57 % yield of bis(MM)N, under relatively mild conditions (4 h, 120 °C).

These observations indicated that dimethoxymethane was more reactive as an alkoxyalkylating reagent than diethoxymethane (thought to be due to the shape selectivity of the zeolite). In view of this, it was decided to carry out the methoxymethylation of 2-EMN over HM, in an attempt to increase the conversion

of 2-EMN and give a high yield of the disubstituted product (ethoxymethyl)(methoxymethyl)naphthalene.

It was hoped that the high selectivity observed in the ethoxymethylation of 2-EMN (only one bis(EM)N isomer observed) would be retained to give a high yield of (2-ethoxymethyl)-6-(methoxymethyl)naphthalene.

The fact that the expected product comprised a naphthalene ring incorporating a methoxymethyl substitutent and an ethoxymethyl substituent would not have any implications with regards to producing highly pure PEN. If this route were adopted in the production of PEN, there would be a requirement for the disposal of two waste alcohols as both methanol and ethanol would be produced in the final polymerisation step with ethylene glycol. Only one waste alcohol would be generated if producing PEN from bis(MM)N or bis(EM)N (methanol and ethanol, respectively).

5.2.9 Separation of bis(EM)N from the crude mixture in an attempt to determine which isomer was observed

5.2.9.1 Isolation of bis(EM)N from the crude reaction mixture.

The crude reaction mixture was subjected to kugelrorh distillation and bis(EM)N was separated as a yellow oil (confirmed by GC analysis). The pure compound was subjected to analysis by mass spectrometry (confirmed relative molecular mass of 244) and NMR.

5.2.10 Characterisation of bis(EM)N

5.2.10.1 NMR analysis

Three signals were observed in the aliphatic region; a triplet at δ 1.23 integrating for six protons, a quartet at δ 3.58 integrating for four protons and a singlet at δ 4.55 integrating for four protons, corresponding to four CH_2 groups and two CH_3

groups of the ethoxymethyl substituents. The number of signals observed suggested that the bis(EM)N isomer was symmetrical. If the isomer were non-symmetrical one would have expected twice as many signals (i.e. four signals for each CH_2 group and two signals for each CH_3 group).

Three signals were observed in the aromatic region; a doublet at δ 7.75 integrating for two protons, a singlet at δ 7.74 integrating for two protons and a doublet at 7.45 integrating for two protons, corresponding to the six aromatic protons of the naphthalene ring. Again, this suggested that the bis(EM)N isomer was symmetrical. If the bis(EM)N isomer were non-symmetrical, one would have expected one signal for each aromatic proton (six signals).

The coupling pattern observed in the aromatic region was characteristic of a **2,6-** disubstituted naphthalene ring or a **2,7-** disubstituted naphthalene ring (both would give the same NMR coupling pattern) (see Figure **5.2.1** and **5.2.2** for structures of 2,6- and 2,7-bis(EM)N). Therefore, it was impossible to determine if the bis(EM)N isomer corresponded to 2,6-bis(MM)N or 2,7-bis(MM)N using NMR analysis. Due to time constraints, the bis(EM)N isomer was not sent away for further investigation (oxidation reaction) as with 2,6-bis(MM)N (Section **3.3.4.2** in Part 3 of Chapter 3). However, one can speculate that the isomer was the desired **2,6-bis(EM)N**, based on results observed in the optimised reaction of dimethoxymethane and naphthalene over HM, where 2,6-bis(MM)N was the major isomer observed (Part 3 of Chapter 3).

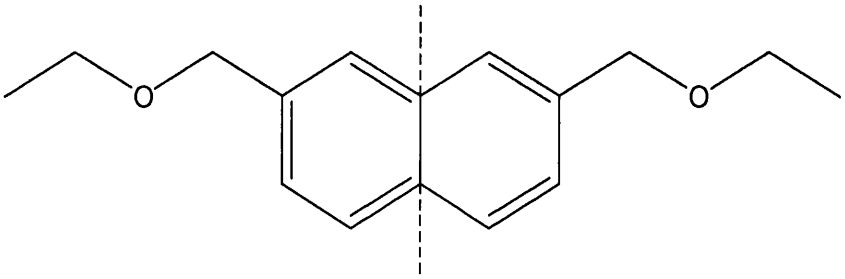


Figure 5.2.1: Structure of 2,7-bis(EM)N, showing a plane of symmetry

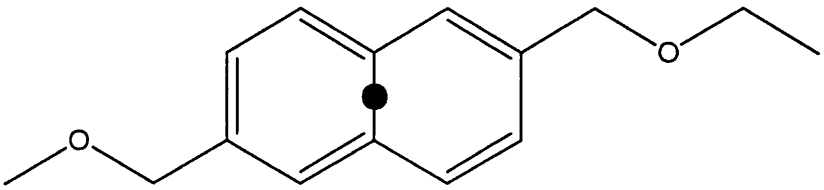


Figure 5.2.2: Structure of 2,6-bis(EM)N, showing a centre of symmetry

5.2.11 Methoxymethylation of 2-EMN over HM under optimised conditions (reaction of dimethoxymethane and 2-EMN catalysed by HM).

2-(Ethoxymethyl)naphthalene (10 mmol) was stirred with dimethoxymethane (758 mmol) in the presence of HM (Si/Al 40, 4 g) under optimised conditions (170 °C, 4 h). The reaction was carried out using the same procedure as described in Section **3.1.11** in Part 1 of Chapter 3.

GC analysis of the reaction mixture showed that several products were generated during the reaction between dimethoxymethane and 2-EMN over HM. The reaction mixture was subjected to GCMS analysis to determine the molecular weight of each product. A correlation between the retention times of the products from GC analysis, the molecular weight of each compound from GCMS analysis, and the corresponding compounds are reported in Table 5.2.6.

Samples of the available pure compounds were co-injected with the reaction mixture for confirmation. The isomers of bis(MM)N with retentions of 41.2 min, 41.5 min and 44.1 min were not available and neither was any isomer of (2-ethoxymethyl)-6-(methoxymethyl)naphthalene or bis(EM)N. In these cases therefore, suggested compounds are speculations based purely on the relative molecular masses observed.

Compounds observed in the reaction mixture included; 1- and 2-(methoxymethyl)naphthalenes with retention times of 35.8 min and 36.1 min, respectively, recovered 2-EMN, with a retention time of 38.2 min, four isomers of bis(MM)N with retention times of 41.2 min, 41.5 min, 44.1 min, and 44.3 min, two isomers of (ethoxymethyl)(methoxymethyl)naphthalene with retention times of 47.2 min and 48.5 min, and a bis(EM)N isomer with a retention time of 44.3 min.

It was noted that the isomers of bis(MM)N with retention times of 41.2 min and 41.5 min were not observed in the methoxymethylation of 2-MMN or naphthalene over HM. Furthermore, the 2,3- bis(MM)N with a retention time of 39.4 min observed in the methoxymethylation of 2-MMN and naphthalene over Hβ, was not observed in the methoxymethylation of 2-EMN over HM. However, the bis(MM)N isomer at 44.1 min was probably 2,7-bis(MM)N.

Table 5.2.6: Correlation of GC retention times, relative molecular masses and suggested compounds, generated in the reaction between dimethoxymethane and 2-ethoxymethylnaphthalene over HM zeolite under optimised conditions.

Retention Time (min)	Mr (Daltons)	Corresponding Compound
35.8	172	1-MMN
36.1	172	2-MMN
38.2	186	2-EMN
41.2	216	a bis(MM)N isomer
41.5	216	a bis(MM)N isomer
44.1	216	a bis(MM)N isomer
44.3	216	2,6-bis(MM)N
46.7	244	a bis(EM)N isomer
47.2	230	an (ethoxymethyl)(methoxymethyl)naphthalene isomer
48.5	230	an (ethoxymethyl)(methoxymethyl)naphthalene isomer

The products observed were very interesting, as one would not expect to see 1-MMN, 2-MMN, bis(MM)N or bis(EM)N products in a reaction between dimethoxymethane and 2-EMN. However, exchange of alkoxy groups between 2-EMN and DMM under zeolite catalysis would lead to 2-MMN and ethoxymethoxymethane and/ or diethoxymethane. The latter two compounds provide a source for formation of bis(EM)N, while the 2-MMN could give rise to a series of bis(MM)N isomers. The appearance of 1-MMN must imply some reversibility of the

reactions, or direct isomerisation of 2-MMN under zeolite catalysis under these reaction conditions.

The percentage yield of each product was calculated and the results are reported in Table 5.2.7. An estimated response factor was used when calculating the yield of (ethoxymethyl)(methoxymethyl)naphthalenes, since a pure sample was not available. The response factor was based on response factors calculated for bis(MM)N and bis(EM)N, where pure samples were available.

2,6-Bis(MM)N had a retention time of 44.3 min and a response factor of 0.38 (response factors were calculated using the equations set out in Section **3.1.14**in Part 1 of Chapter 3), while bis(EM)N had a retention time of 46.7 min and a response factor of 0.22. The two isomers of (ethoxymethyl)(methoxymethyl)naphthalene had retention times of 47.2 min and 48 5 min, and a response factor of 0.18 was estimated.

Table 5.2.7: Comparson of the products and yields in the methoxymethylation and ethoxymethylation of 2-ethoxymethylnaphthalene over HM, under optimised conditions[a]

	Methoxymethylation of 2-EMN over HM	**Optimised Ethoxymethylation of 2-EMN over HM**
Swansea experiment code	MMN-2-EMN	Di-EMN170
EMN recovery (%)	3	66
MMN (%)	2	2
Et(MMN) (%)	0	5
Bis(MM)N (%)	17	0
Bis(EM)N (%)+A1	4	26
(ethoxymethyl,methoxymethyl)naphthalene	13	0
Total (%)	39	99

[a] 4 h stirred mini reactor reactions at 170 °C under self generated pressure; HM (Si/Al 40, 4 g), 2-EMN (1.86 g, 10 mmol), dimethoxymethane (57.64 g, 758 mmol).

5.2.12 Comparing the ethoxymethylation and methoxymethylation of 2-EMN over HM, under optimised conditions.

As predicted, the alkoxymethylation of 2-EMN occurred to a much higher extent in the reaction where dimethoxymethane was the alkoxyalkylating agent, compared to the reaction where diethoxymethane was the alkoxyalkating agent, with 97 % conversion and 34 % conversion being observed, respectively. The same yield of MMN was observed (2 %) in both the methoxymethylation of 2-EMN and the ethoxymethylation of 2-EMN over HM. Et(MMN) was not observed in the methoxymethylation of 2-EMN, whereas a 5 % yield was observed in the ethoxymethylation of 2-EMN.

With regards to the disubstituted products, the expected products (ethoxymethyl)(methoxymethyl)naphthalenes (two isomers) were observed in 13 % yield in the methoxymethylation of 2-EMN. Bis(MM)Ns (four isomers) were also observed in 17 % yield in the methoxymethylation of 2-EMN. Interestingly, bis(EM)N was observed in a 4 % yield in the methoxymethylation of 2-EMN, where there was no apparent source of additional ethoxymethyl groups. Bis(EM)N was observed in 26 % yield in the ethoxymethylation of 2-EMN, but this is more readily understandable.

The high conversion (98 %) observed in the methoxymethylation of 2-EMN was not reflected in the yield of products observed. Rather, a low recovery of material from the reaction mixture ensued. Only 33 % of material was recovered from the reaction mixture, which was thought to be due to further reaction of the disubstituted compounds (with either 2-EMN, DMM or other disubstituted compounds, for example) to give high molecular weight products (coke) that could get stuck in the pores of zeolite, resulting in a low mass balance.

In summary, the methoxymethylation of 2-EMN over HM gave a complicated mixture of products in addition to the mono-methoxymethylated products of 2-EMN (two products were observed the ethoxymethylation of 2-EMN over HM, where the major product was a bis(EM)N isomer and the other was ethyl(ethoxymethyl)naphthalene). One can conclude that a significantly higher conversion of 2-EMN was observed in the methoxymethylation of 2-EMN compared to the ethoxymethylation of 2-EMN (though not reflected in the yield of desired product), but that the reaction with diethoxymethane was more selective (only one isomer of bis(EM)N observed, whereas 4 isomers of bis(MM)N in addition to other disubstituted products were observed in the reaction with dimethoxymethane). The

recovery of material from the reaction mixture observed in the ethoxymethylation of 2-EMN over HM was also much higher, compared to the methoxymethylation of 2-EMN over HM.

5.2.13 Summary and Conclusions

It was decided to investigate the reaction between diethoxymethane and 2-EMN over zeolite HM, in an attempt to produce 2,6-bis(EM)N selectively. Bis(EM)N (1 isomer) was indeed observed in 3 % yield in an initial reaction, under relatively mild conditions (4 h, 120 °C). This reaction was optimised and several reaction parameters were varied.

The reaction of diethoxymethane and 2-EMN over HM did not reach completion even under forcing conditions (possibly due to size constraints of HM, leading to the slow diffusion of the bulky diethoxymethane reagent, in turn giving rise to a slow rate of reaction and poor conversion).

In addition, when too much force was used the yield of the desired product and the recovery of the material from the reaction mixture both decreased (thought to be due to secondary reactions which produced high molecular weight compounds that were non-retractable from the zeolite framework). Furthermore, unwanted side products were also observed. The general trends are reported below.

Increasing reaction temperature

Increasing the reaction temperature resulted in an increased conversion, increased yield of MMN*, increased yield of Et(MMN) and increased yield of bis(EM)N.

Increasing reaction time

Increasing the reaction time resulted in an increased conversion and increased yield of MMN*. The yield of bis(EM)N decreased and the yield of Et(MMN) remained the same.

Increasing the amount of HM

Increasing the amount of HM resulted in an increased conversion, increased yield of Et(MMN) and decreased yield of MMN*. The recovery of material from the reaction mixture decreased and the yield of bis(EM)N was largely unaffected.

Application of Hβ to optimised ethoxymethylation of 2-EMN

Applying Hβ instead of HM to the optimised reaction between naphthalene and diethoxymethane resulted in a decreased conversion, decreased yield of Et(MMN), decreased yield of bis(EM)N and increased yield of MMN*.

** It was noted that the 2/1 ratio of 2-MMN and 1-MMN was between 1 and 2 in all of the reactions mentioned above.*

Methoxymethylation of 2-EMN over HM

In the methoxymethylation of 2-EMN, the conversion of 2-EMN was higher and the recovery of material from the reaction mixture lower than the comparable ethoxymethylation of 2-EMN under the same conditions. In addition, the reaction mixture was more complicated and several side products were observed.

The best result so far was a 26 % yield of bis(EM)N (thought to be **2,6-bis(EM)N**). This was achieved with 2-EMN (10 mmol), diethoxymethane (535 mmol) and HM (Si/Al 40, 4 g) under optimised conditions (4 h, 170 °C). A 2 % yield of MMN and 5 % of Et(MMN) were also observed in this reaction.

Comparing the ethoxymethylation of 2-EMN and the methoxymethylation of 2-MMN, over HM.

In conclusion, a higher conversion and higher yield of bis(MM)N was observed in the methoxymethylation of 2-MMN (63 % and 57 %, respectively) under relatively mild conditions (4 h, 120 °C), compared to the analogous ethoxymethylation of 2-EMN where a 34 % conversion and 26 % yield of bis(EM)N were observed using more force (4 h, 170 °C). However, the ethoxymethylation of 2-EMN was more selective regarding the second alkoxyalkyation, with only one isomer of bis(EM)N being observed, whereas three isomers of bis(MM)N were observed in the methoxymethylation of 2-MMN (2,6-bis(MM)N being the major isomer).

5.2.14 Experimental

The reaction procedure for alkoxyalkylation of naphthalene and substituted naphthalenes was identical to that set out in Section **3.1.11** in Part 1 of Chapter 3. Any exceptions are described in the footnotes under the relevant results tables.

5.2.14.1 Synthesis of 2-ethoxymethylnaphthalene from 2-naphthalenemethanol and ethyl iodide

tert-Butyllithium (7.0 ml, 12 mmol) was introduced to a stirred solution of 2-naphthalenemethanol (2.0 g, 12 mmol) in dry THF (40 ml) in a 200 ml round bottomed flask contained in an ice bath. The reaction mixture was stirred at 0 °C for 1 h under argon, EtI (10 ml, 125 mmol) was then introduced. The reaction mixture was stirred for a further 4 h at 40 °C under argon. The product mixture was treated with saturated ammonium chloride solution (20 ml). The organic layer was separated and the aqueous layer was extracted with diethylether (3 x 20 ml). The organic fractions were combined, washed with water (3 x 20 ml) and dried over magnesium sulfate. Solvents were removed at the pump to yield a yellow oil (2.14 g). The oil comprised a single component by GC analysis, and it corresponded to 2-ethoxymethylnaphthalene (96 %).

5.2.15 GC analysis

GC analysis of product mixtures was carried out under the same conditions as described in **Figure 3.1.6** in Part 1 of Chapter 3. The GC traces of the product mixtures under these conditions gave the following results. 2-Ethoxymethylnaphthalene had a retention time (Rt) of 38.2 min, tetradecane had a Rt of 30.5 min. Analysis of reactions of 2-ethoxymethylnaphthalene and diethoxymethane gave peaks with retention times of 35.8 min and 36.1 min corresponding to 1- and 2-(methoxymethyl)naphthalenes, respectively. Peaks with retention times of 40.3 min and 46.7 min corresponded to an ethyl(methoxymethyl)naphthalene isomer and a bis(ethoxymethyl)naphthalene isomer, respectively.

Analysis of reactions of 2-ethoxymethylnaphthalene and dimethoxymethane gave peaks with retention times of 35.8 min and 36.1 min corresponding to 1- and 2-(methoxymethyl)naphthalenes, respectively. Peaks with retention times of 41.2 min, 41.5 min, 44.1 min and 44.3 min were also observed corresponding to isomers of bis(methoxymethyl)naphthalene (isomer with retention time of 44.3 min corresponded to 2,6-bis(MM)N). A peak with retention time 46.7 min corresponded to bis(ethoxymethyl)naphthalene, and peaks with retention times of 47.2 min and 48.5 min corresponded to isomers of (ethoxymethyl)(methoxymethyl)naphthalene.

5.2.15.1 Quantification of products

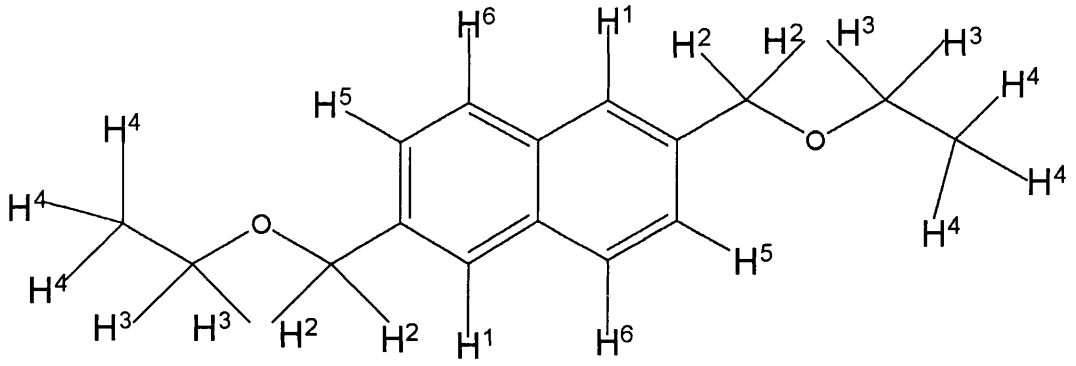
Response factors for reagents and products generated during the reactions were calculated using the procedure outlined in Section **3.1.12** in Part 1 of Chapter 3 unless stated. The relative amounts of the products formed in each reaction were then quantified. Crude products were made up in a solution of known volume along with a known amount of internal standard and injected into the GC for analysis.

5.2.16 Analytical data

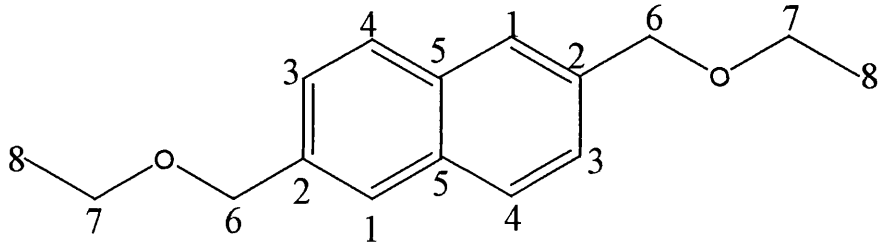
Bis(ethoxymethyl)naphthalene

*(Thought to be **2,6**-bis(ethoxymethyl)naphthalene)*

NMR: ^{1}H and ^{13}C, $CDCl_3$ as solvent



$\delta^{1}H$: 7.75 (2H, d, J = 8 Hz, H^{6}), 7.74 (2H, s, H^{1}), 7.45 (2H, d, J = 8 Hz, H^{5}), 4.55 (4H, s, H^{2}), 3.58 (4H, q, J = 7 Hz, H^{3}), 1.23 (6H, t, J = 7 Hz, H^{4})

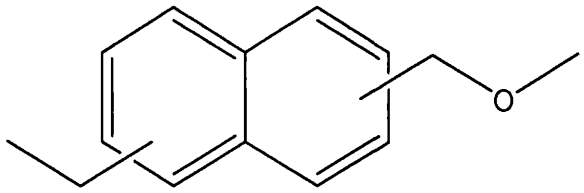


δ^{13}**C:** 128.5 (C^{2}), 128.3 (C^{5}), 126.7 (C^{4}), 126.4 (C^{3}), 126.1 (C^{1}), 73.2 (C^{6}), 66.2 (C^{7}), 15.7 (C^{8}).

MS: (from GCMS)

EI m/z (% abundance): 244 (66) [M^{+}], 200 (75), 155 (78), 141 (100), 128 (33).

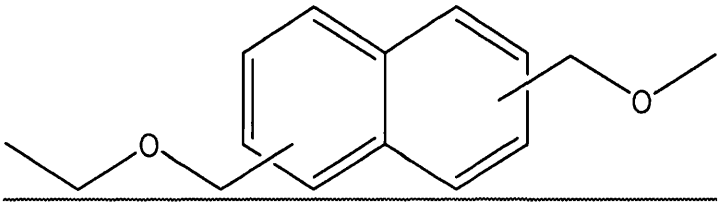
Ethyl(methoxymethyl)naphthalene



MS: (from GCMS)

EI m/z (% abundance): 200 (50) [M^+], 184 (62), 169 (63), 156 (100), 141 (51).

(Ethoxymethyl)(methoxymethyl)naphthalene



MS: (from GCMS)

EI m/z (% abundance): 230 (88) [M^+], 215 (47), 198 (100), 183 (35), 167 (65).

Chapter 6

Final Conclusions

6.1.1 Final Conclusions

2,6-Dimethylnaphthalene (2,6-DMN) is a very profitable intermediate in the commercial production of polyethylenenaphthalate (PEN). In view of this, many industrial companies including BP Amoco, Mitsibushi and Optatech, have developed processes for producing 2,6-DMN. However, these processes are severely limited, in terms of the selectivity and yield of the final product.

In view of this, it was decided to investigate an alternative method for synthesising 2,6-DMN and analogues in an attempt to overcome these limitations and improve the yield and selectivity of the desired product. Two possible approaches were investigated in this body of work. The first involved the selective build up of an appropriate monocyclic compound to give the desired 2,6-DMN. The second involved the selective alkoxyalkylation of the naphthalene ring.

The synthesis of 2,6-DMN from *p*-xylene and crotonic acid (three stages) was attempted with little success. In the first stage the zeolite catalysts employed were not sufficiently active to facilitate the reaction and the aromatic ketone was not observed. The second stage of the reaction was also found to be unsuccessful as the major product generated was an undesirable side product containing a 5-membered ring, rather than the desired tetralone intermediate. Therefore, 2,6-DMN could not be generated.

The second approach involved the alkoxyalkylation of naphthalene. It was thought that this method could improve on the direct alkylation of naphthalene by introducing an alkoxy functionality to the substituent. The inclusion of an oxygen atom could eliminate an oxidation step in the production of PEN.

In the methoxymethylation of naphthalene over HM under optimised conditions (4 h, 120 °C, under self generated pressure) a 45 % yield of

mono(methoxymethyl)naphthalene with a 2/1 of 3.0 and a 45 % yield of bis(methoxymethyl)naphthalene with a 2,6/2,7-ratio of 17.0 were observed.

In the ethoxymethylation of naphthalene over HM under optimised conditions a 19 % yield of mono(ethoxymethyl)naphthalene with a 2/1 of 9.9 was observed. Bis(EM)N was not observed.

A reaction was also carried out between 2-(ethoxymethyl)naphthalene and diethoxymethane, where bis(EM)N was observed in a 26 % yield. Only one bis(EM)N isomer, which was thought to be the desired 2,6- isomer, was observed.

The significant difference in the conversion between the methoxymethylation and ethoxymethylation reactions was thought to be due to the interaction of the reagents with the zeolite. Diethoxymethane is a bulkier reagent than dimethoxymethane, therefore the rate of diffusion of DEM into the pores of HM may have been slower than the rate of diffusion of DMM into the pores of HM. Consequently, a slower reaction and a lower conversion of naphthalene would be observed in the ethoxymethylation of naphthalene compared to the methoxymethylation of naphthalene.

The high selectivity observed in the ethoxymethylation reactions can be explained in terms of the shape selectivity of the HM catalyst. 1-EMN is less linear than 2-EMN, therefore the channels within the HM framework may have facilitated the β substitution of naphthalene rather than the α substitution of naphthalene. Thus, a greater amount of 2-EMN than 1-EMN would be observed.

The reaction between dimethoxymethane and naphthalene was less selective, with a 2/1 ratio of 3.0 being observed in the optimised reaction (although a higher selectivity was observed in the second substitution where 2,6-bis(MM)N was the major isomer).

This can be explained in similar terms; 1-MMN is less linear than 2-MMN and therefore a higher proportion of 2-MMN was observed compared to 1-MMN. However, the 2/1 ratio of MMN was much lower than the 2/1 ratio of EMN. This is probably because MMN is a smaller molecule than EMN, therefore the formation of 1-EMN would have been more restricted by the size constraints of the zeolite than the formation of 1-MMN. In other words, the zeolite was more shape selective towards the 2-EMN isomer in the ethoxymethylation of naphthalene, compared to the 2-MMN isomer in the methoxymethylation of naphthalene.

In summary, both the ethoxymethylation and methoxymethylation of naphthalene have their relative advantages and disadvantages as routes for producing an intermediate in the synthesis of PEN. The ethoxymethylation of naphthalene would be a superior method if the high selectivity achieved was coupled with an increased conversion of naphthalene, to give high yields of EMN and bis(EM)N. On the other hand, the methoxymethylation of naphthalene would be a superior method if the selectivity of the initial substitution could be increased, or if a method could be developed in order to achieve a good separation of the 1-MMN and 2-MMN isomers.

6.1.2 Comparison of the best alkoxyalkylation reaction of naphthalene with the current routes for producing an intermediate to be used in the synthesis of PEN

As already mentioned, the best results so far were achieved in the optimised methoxymethylation of naphthalene over zeolite HM. These results were reported in Part 2 of Chapter 3 (Table 3.2.11) and are reported again in Table 6.1.1

Table 6.1.1: Table to show the best alkoxyalkylation of naphthalene results achieved in the optimised reaction of naphthalene and dimethoxymethane over HM (Si/Al 40) zeolite[a]

Best Results	
Swansea experiment code	DMM+HM(40)8g
Naphthalene recovery (%)	9
Methylnaphthalenes (%)	0
MMN (%)	45
2/1 ratio	3.0
Bis(MM)N (%)	45
2,6/2,7 ratio	17.0
Total (%)	99

[a] 4 h stirred mini reactor reactions at 120 °C under self generated pressure; catalyst (HM Si/Al 40), naphthalene (1.28 g, 10 mmol), dimethoxymethane (57.6 g, 758 mmol).

A 91 % naphthalene conversion was achieved with a 45 % yield of mono(methoxymethyl)naphthalene (2/1 of 3.0) and a 45 % yield of bis(methoxymethyl)naphthalene (2,6/2,7-ratio of 17.0). These results were extremely exciting and it was conceivable that 100 % conversion could be achieved, to give the maximum yield of MMN and bis(MM)N, if the reaction was optimised further (e.g. increase in reaction time, increase in catalyst amount).

If this reaction was developed further and used commercially to produce an intermediate for the synthesis of PEN, it would hold many advantages over the current routes for producing 2,6-DMN (as described in Part 3 of Chapter 1) in terms of the high conversion, high reaction selectivity, high yield of desired final product, use of a *environmentally friendly* zeolite catalyst and cheap readily available reagents and limited reaction steps required.

One can conclude that if this reaction was developed further it would provide an excellent alternative and be a serious competitor for current methodology employed for producing suitable intermediates in the commercial production of PEN.

At present, Davy Process Technology are commercialising a process for the small scale production of 2,6-(methoxymethyl)naphthalene to be used in the commercial synthesis of PEN, based on my results reported in Table 6.1.1. The work contained in Chapters 3, 4 and 5 is also reported in the patent literature.

Appendix

Instrumentation

GC

For the GC analysis of the reactions carried out in **Chapter 2**, a Phillips PU 4400 gas chromatograph fitted with a 100 % polyethylene glycol (15 m, 0.53 mm ID, film thickness 0.5 μm) capillary column was used.

For the GC analysis of the reactions carried out in **Chapters 3, 4 and 5**, a Phillips PU 4400 gas chromatograph fitted with a 95 % dimethylpolysiloxane 5 % phenol (30 m, 0.32 nm ID, film thickness 1 μm) capillary column was used.

GCMS

GCMS analysis was carried out using the electron impact (EI) ionisation technique on a Fisons GC8000 gas chromatograph fitted with a 95 % dimethylpolysiloxane 5 % phenol (30 m, 0.32 mm ID, film thickness 1μm) capillary column, directly interfaced with a Fisons Masslab MD800 low-resolution GCMS instrument. Mass charge ratios are given in Daltons followed by their percentage relative abundance.

MS

Mass spectra were recorded on either a VG 12-250 low resolution quadrupole instrument or a VG Micromass Quattro II instrument.

Accurate Mass

Accurate mass measurements were carried on either a ZAB-E high resolution double-focusing instrument or a Finnigan Mat 900 instrument.

TLC

TLC analysis was carried out on Merck 5785 Kiesegel $60F_{254}$ fluorescent plates

NMR

NMR spectra were run on a Bruker AC-400 Fourier Transform spectrometer at 400 MHz for proton and 100 MHz for carbon spectra. Samples were run in $CDCl_3$ where tetramethylsilane was used as the internal standard. Chemical shifts (δ) are expressed in ppm (parts per million). A key for the coupling patterns is given below.

s = singlet

d = doublet

dd = double doublet

dq = double quartet

t = triplet

m = multiplet

Br = Broad signal

Chemical suppliers

All chemicals were obtained from Aldrich. Zeolites were either obtained from sudie chemie or kindly donated by DPT. Pure sample of 2-ethoxymethylnaphthalene kindly supplied by DPT.

Purification of solvents

THF was distilled from sodium benzophenone ketyl. Other solvents were purified by standard procedures.[1], [2]

References

1. D. D. Armarego,W. L. F. Perrin, *Purification of organic chemicals.*, pergamons.

2. Vogel's textbook of practical organic chemistry., 5th Edn, Longman, Harlow 1989.